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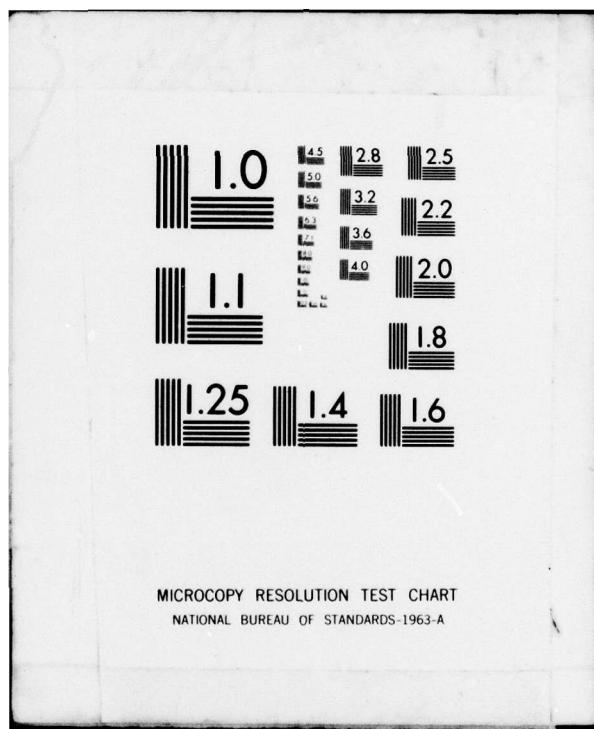
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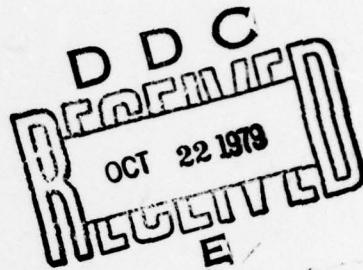
OPTIMIZATION OF PT-DOPED KOCITE^R ELECTRODES

IN H₃PO₄ FUEL CELLS

by

L. B. Welsh, R. W. Leyerle

May, 1979



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Different types of Kocite-derived electrocatalysts were produced by first leaching of the alumina substrate from a Kocite material and then impregnating the resulting pyropolymer structure with platinum using one of several different techniques. Electrocatalysts fabricated by these techniques normally have a 650 m²/g surface area and a 15 wt-% platinum loading.

PTFE-bonded gas diffusion electrodes, with a porous graphite-paper backing were fabricated from these electrocatalysts by both machine-calendering and sheet molding techniques. Typical Kocite electrode platinum loadings were 0.6 mg/cm². Model fuel cell test results were normally obtained at 180°C with air cathodes and H₂ anodes operated at atmospheric pressure. Recent cell testing stressed the use of Kocite electrodes as both anodes and cathodes while testing large enough numbers of cells to determine cell performance reproducibility with current cell assembly techniques and hardware. Electrodes produced from the best electrocatalysts prepared during this program have operated in excess of 5000 hrs. with a peak performance of 630 mV at 200 mA/cm² and 180°C.

¹"Kocite" is a registered trademark of UOP Inc.

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I. INTRODUCTION

1.1 Objectives

The objective of this program was to optimize the performance of low-cost air and fuel electrodes fabricated from platinum-impregnated UOP Kocite^R materials for use in phosphoric-acid-electrolyte fuel cells operating at temperatures near 180°C. To accomplish this objective, various Kocite-derived electrocatalysts were produced and fabricated into state-of-the-art fuel cell electrodes. These electrodes were tested as cathodes and anodes in model fuel cells. The cell testing determined both the performance level and long term endurance attainable with Kocite electrodes.

The sole criteria for evaluating Kocite-derived electrocatalysts was the ability of a specified amount of Pt, on the support and within the electrode structure, to produce a certain voltage level at a set operating current density. This performance goal was raised several times during this program. Over most of this program, the performance goal of any given contract period was met or exceeded. However, the most recent goal of 0.4 mg/cm² Pt-loaded Kocite electrodes giving 650 mV (cell terminal voltage) when tested on air at 180°C and 200 mA/cm² has not been reached. This goal is believed to substantially exceed current state-of-the-art performance levels of low loaded gas diffusion electrodes in atmospheric pressure phosphoric acid electrolyte fuel cells.

This report summarizes the results obtained since the inception of the contract in September, 1975. This includes both a report of the results obtained since the last report in August, 1978 and a review of earlier results. Kocite-derived electrocatalyst formulations prepared during the contract and the performance levels attained with Kocite electrodes made from these electrocatalysts will be discussed, along with recommendations for future research and development.

1.2 Background

The program discussed here followed an evaluation of the performance of Kocite materials in fuel cell electrodes for phosphoric-acid electrolyte fuel cells completed under USAMERDC contract number DAAK02-75-C-0011.¹ The program organization established under the earlier contract was maintained throughout the program. This involved a joint pro-

¹L. B. Welsh, R. W. Leyerle, G. L. Hervert and K. J. Youtsey, "Carbonaceous Catalysts for H₃PO₄ Fuel Cells", MERDC Contract DAAK02-75-C-0011, Final Technical Report, September, 1975.

gram with UOP as the prime contractor and Energy Research Corporation (ERC, a subsidiary of St. Joe Minerals Corporation) as subcontractor. A broad division of effort was made on the basis of the UOP capability to produce Pt-impregnated Kocite-derived electrocatalysts and the ERC capability to fabricate and optimize electrode structures. Testing and diagnostic evaluations of these electrodes were carried out jointly by UOP and ERC.

The basis on which these contractual efforts were initiated and continued was the development at UOP Inc. of Kocite^R materials, which had the necessary properties to serve as possible supports or extenders of catalytically active materials (noble metals, transition metals, etc.). Kocite materials are composite structures consisting of a thin-film, semiconducting pyropolymer chemically bonded to the surface of an electrically-insulating, high-surface-area, refractory substrate. The materials used to produce Kocite can vary widely, but commonly include gamma alumina as the refractory substrate and hydrocarbons such as cyclohexane or benzene as the pyrolyzable material or pyropolymer precursor. Pyrolysis temperatures are commonly in the range of 400 to 900°C. The electrical conductivity of these materials can be varied in a controlled manner by adjusting one or more of the following parameters: (a) substrate composition and surface area, (b) pyrolyzable material, and (c) reaction conditions (e.g., reaction time, temperature, ambient gases). The characteristics of the Kocite materials used for this program are summarized in Section II.

1.3 Summary of Program Results

In this section the most important results obtained during the contract will be briefly summarized. These results will be discussed in greater depth in Sections II to V.

1.3.1 Kocite Materials

During this contract a wide variety of Kocite materials were evaluated as electrocatalyst supports. This evaluation led to the choice of a Kocite material using Alcoa's Hydral 705 as the standard starting substrate material on the basis of electrode performance results. Relevant properties of this type of Kocite material are given in Table I. The majority of Kocite materials used during the last year of this contract were of this type.

Table I
Typical Kocite Material Properties

Substrate	Hydral 705
Pyropolymer Precursor	Benzene
Carbon Content	~25 wt-%
Resistivity at 25°C	~0.1 Ω-cm
Surface Area	~80 m ² /g
Average Pore Diameter	~6 nm
Average Particle Diameter	~0.5 μm

1.3.2 Kocite-Derived Electrocatalysts

During the early portions of this program, all electrocatalysts were prepared by the platinum impregnation of Kocite materials.²⁻⁴ However, as a result of the discovery that the alumina substrate was leached from small Kocite particles by phosphoric acid during fuel cell operation, it was believed that improved electrocatalysts could be obtained by leaching the alumina from the Kocite particles prior to platinum impregnation. The resulting Kocite-derived electrocatalysts consist of very small platinum particles supported on a very high-surface-area pyropolymer structure.^{5,6}

²L. B. Welsh, R. W. Leyerle, G. L. Hervert, "Optimization of Pt-Doped Kocite^R Electrodes in H₃PO₄ Fuel Cells", MERADCOM Contract DAAG53-76-C-0014, Interim Technical Report, March, 1976.

³L. B. Welsh, R. W. Leyerle, "Optimization of Pt-Doped Kocite^R Electrodes in H₃PO₄ Fuel Cells", MERADCOM Contract DAAG53-76-C-0014, Interim Technical Report, August, 1976.

⁴L. B. Welsh, R. W. Leyerle, "Optimization of Pt-Doped Kocite^R Electrodes in H₂PO₄ Fuel Cells", MERADCOM Contract DAAG53-76-C-0014, Interim Technical Report, January, 1977.

⁵L. B. Welsh, R. W. Leyerle, "Optimization of Pt-Doped Kocite^R Electrodes in H₃PO₄ Fuel Cells", MERADCOM Contract DAAG53-76-C-0014, Interim Technical Report, January, 1978.

⁶L. B. Welsh, R. W. Leyerle and D. M. Preston, "Optimization of Pt-Doped Kocite^R Electrodes in H₃PO₄ Fuel Cells", MERADCOM Contract DAAG53-76-C-0014, Interim Technical Report, August, 1978.

Various platinum impregnation techniques were used to obtain a good platinum dispersion on the leached Kocite material.^{5,6} Kocite-derived electrocatalysts were produced after impregnating with chloroplatinic acid, platinum diaminedinitrite, platinum acetylacetone, or thiomalic acid-chloroplatinic acid mixtures. In addition electrocatalysts were produced by impregnating the alumina substrate prior to pyropolymer deposition, impregnating prior to leaching the Kocite material, or impregnating subsequent to the leaching step.^{5,6} The best platinum dispersions and electrocatalyst performance were obtained by the platinum impregnation of the leached Kocite material using platinum diaminedinitrite.

In the early phases of the program electrocatalysts were produced having platinum contents from 2 to 20 wt-% of the Kocite material. Electrocatalyst and electrode performance indicated that optimum results were obtained with a platinum content near 15 wt-% of the leached Kocite material. Some of the characteristics of the best Kocite-derived electrocatalysts are listed in Table II.

Table II

Kocite-Derived Electrocatalyst Properties

Platinum Content	15 wt-%
Carbon Content	80 wt-%
Aluminum Content	~0.1 wt-%
Phosphorus Content	~0.5 wt-%
Platinum Source	$\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$
Average Platinum Particle Size	~2.0 nm
Surface Area	625 m^2/g
Average Pore Diameter	7.0 nm
Average Particle Diameter	~0.3 μm

1.3.3 Kocite Electrodes

The gas diffusion Kocite electrodes used in this program were made by techniques developed at ERC. Initially all electrode catalyst layers were fabricated by hand rolling the catalyst layer.² Later, both machine rolling and sheet molding processes were used.^{5,6} The most reproducible electrodes were obtained by the machine rolling process. The catalyst layer was pressure bonded to a porous carbon paper backing to complete the electrode.

Substantial efforts were made to optimize the Kocite electrode catalyst layer as to PTFE content, porosity, catalyst layer thickness, etc.⁴⁻⁶ The most important variable appeared to be the PTFE content with optimal results being obtained for ~45 wt-% teflon.

Very low platinum loaded Kocite electrodes were used during the initial phases of this contract. For most of the contract period Pt loadings were restricted to 0.20 to 0.65 mg/cm². During the last year only electrodes with 0.50 to 0.65 mg/cm² Pt were normally produced, consistent with Pt loadings of commercially produced electrodes with carbon black supports.

1.3.4 Kocite Electrode Testing

Throughout this contract, Kocite electrodes were tested primarily as 2"x2" cathodes in graphite hardware supplied by ERC. Until the last year of the contract, 2 mg/cm² Pt-loaded Pt-black counter electrodes were used. In the last year Kocite electrodes were used as both the cathode and anode of the cells.

Initially cells were run on air or oxygen versus 100% hydrogen at 140°C. As the program progressed the cell temperatures were raised and finally set at 180°C.

1.3.5 Kocite Electrode Performance

As a result of this electrocatalyst and electrode optimization program, the performance of the Kocite electrodes has steadily improved. Initially, the best cell terminal voltage obtained was ~570 mV at 100 ma/cm² and 180°C.² The best cell terminal voltage obtained by the end of the program was 630-640 mV at 200 ma/cm² and 180°C. The best reproducible cell performance results obtained with the best electrocatalyst batches produced during the program fell in the range indicated in Table III.

Table III
Best Air/H₂ Cell Performance Results

Current Density (ma/cm ²)	100	200
Terminal Cell Voltage (mV)	660-690	600-630
Oxygen Gain (mV)	50-60	60-70

Considerable electrode testing was performed to determine both the reproducibility of electrode performance and electrode endurance. Electrode performance reproducibility improved dramatically during the program and appeared to be reasonable by the end of the contract period. Electrode and electrocatalyst endurance were very good with the best cells performing at a terminal voltage of 570 mV on air at 200 ma/cm² in excess of 5000 hours.

A detailed discussion of these results is presented in the following sections. The review of earlier results and the presentation of the most recent results are discussed in separate subsections.

II. PREPARATION AND LEACHING OF KOCITE MATERIALS

2.1 Kocite Materials (September, 1975-August, 1978)

In this section the properties of the most significant Kocite materials prepared prior to the last Interim Technical Report are summarized and some of the characteristics of these materials relevant to their H_3PO_4 fuel cell applications are described. Kocite materials prepared and used since the last Interim Technical Report will be discussed in Section 2.2.

During the program the Kocite materials were prepared in a rotary kiln in batch sizes in excess of 200 grams. Uniform pyropolymer deposition was accomplished by alumina particle-hydrocarbon gas mixing by the rotary motion of the kiln which normally revolved at 20 rpm. Process temperatures were programmer controlled and recorded graphically. All process parameters were carefully controlled to ensure a uniform and reproducible product.

The characteristics of the most important Kocite materials used during this period are given in Table IV. At the inception of this contract a Kaiser alumina substrate was used which had been ground and particle size classified to give an average particle size about $2.2 \mu m$ with a narrow particle size distribution.^{1,2} Because of the gas diffusion losses encountered with this type of substrate during cell operation, other alumina substrates were examined and Alcoa's Hydral 705, with a particle size of $\sim 0.3 \mu m$, was selected as a promising material. Subsequent fuel cell test results indicated significantly lower gas diffusion losses resulted from the use of this substrate with the result that the Hydral 705 has been used as the standard alumina substrate for the duration of the program.²⁻⁶ Toward the end of this contract period efforts began to evaluate Cabot's Alon alumina, a third type of alumina substrate with substantially smaller particle size of $\sim 0.05 \mu m$.⁶

Transmission Electron Micrographs (TEM) of each type of Kocite material are shown in Figures 1, 2 and 3.⁷ The Kaiser-based Kocite particles shown in Figure 1 have an irregular amorphous structure. The TEM of the Hydral 705-based Kocite material (Figure 2) clearly shows this material consists of hexagonally shaped platelets with particle dimensions of ~ 100 to 500 nm in length and width, and ~ 10 nm in thickness. TEM examination of the initial Hydral 705 alumina and the Kocite material prepared from this alumina base shows that no change in particle shape and no apparent change in particle structure occurs during pyropolymer deposition. The Alon-based Kocite particles shown in Figure 3 are much smaller than either the Kaiser or Hydral 705-based Kocite particles and have a narrow particle size distribution.

⁷ TEM results obtained with the cooperation of Professor A. V. Crewe and Mitsuo Ohtsuki at the University of Chicago.

Table IV
Characteristics of Kocite^R Materials*

Batch Number	3289-25	3380-125	3380-156	3289-120	3576-20	3576-60
<u>Preparation</u>						
Substrate	Kaiser	Hydral 705				
Particle Size (10 ³ nm)	~2.2	~0.3	~0.3	~0.3	~0.3	~0.3
Pyropolymer Precursor	C ₆ H ₆					
Pyrolysis Temperature (°C)	900	800	800	840	840	865
<u>Characteristics</u>						
Carbon Content (Wt-%)	36.8	19.0	21.3	21.5	26.6	25.3
Resistivity, ρ, @ 25°C (Ω-cm)	0.051	0.13	0.11	0.17	0.08	0.14
Apparent Bulk Density (g/ml)	0.30	0.32	0.29	0.30	0.27	0.28
Surface Area (m ² /g)	70	80	81	107	77	123
Pore Volume (ml/g)	0.18	0.11	0.11	0.15	0.11	0.17
Average Pore Diameter (nm)	10.3	5.5	5.4	5.6	5.7	5.5

*See references 1-6.

Table IV (Cont'd)
Characteristics of Kocite^R Materials*

Batch Number	3648-66	3648-68	3648-104	3380-65
<u>Preparation</u>				
Substrate	Hydral 705	Hydral 705	Alon	Kaiser
Particle Size (10^3 nm)	~0.3	~0.3	~0.05	2.2
Pyropolymer Precursor	C ₆ H ₆			
Pyrolysis Temperature (°C)	835	842	905	900
<u>Characteristics</u>				
Carbon Content (Wt-%)	24.3	25.3	49	42.2
Resistivity, ρ , @ 25°C ($\Omega\text{-cm}$)	0.064	0.081	0.024	0.006
Apparent Bulk Density (g/ml)	0.29	0.30	0.16	0.85
Surface Area (m^2/g)	73	81	74	64
Pore Volume (ml/g)	0.11	0.10	0.14	0.17
Average Pore Diameter (nm)	6.0	4.9	7.6	10.7

*See references 1-6.

Figure 1

Transmission Electron Micrograph of
Kocite Material Made From Kaiser Substrate Alumina

100 nm



Figure 2

Transmission Electron Micrograph of
Kocite Material Made From Hydral 705 Alumina

100 nm



Figure 3

Transmission Electron Micrograph of
Kocite Material Made From Alon Alumina

100 nm



Nitrogen desorption measurements were used to characterize the pore volume distribution (PVD) of both the Kocite material and the resulting electrocatalyst. The difference in pore volume distribution of Kocite materials attainable by a simple variation of the alumina substrate is shown in Figure 4, where the PVD's of typical Hydral 705, Kaiser and Alon-based Kocite materials are shown. Kaiser-based material has a relatively broad pore volume distribution while Hydral 705-based Kocite material has a distribution sharply peaked near 4.0 nm. Alon-based Kocite material has a peak near 3.0 nm but also a substantial number of pores with diameters greater than 10 nm.

2.2 Kocite Materials (August, 1978-April, 1979)

The characteristics of Kocite materials prepared during this period are summarized in Table V. A number of the standard Hydral 705-based materials were produced as well as an Alon-based material. The 3648-139 Alon-based material was used for electrocatalyst preparation rather than the 3648-104 Alon-based material as it has a carbon content of 25 wt-% similar to the Hydral 705-based Kocite materials. Because of its low apparent bulk density and small particle size, the Alon-based Kocite material was more difficult to process and confine than the standard Hydral 705-based Kocite materials.

2.3 Leached Kocite Materials (September, 1975-August, 1978)

With the realization that the alumina substrate was leached from the electrocatalysts during electrode operation, subsequent electrocatalysts were prepared by leaching the Kocite material prior to electrode fabrication. Various leaching procedures were investigated by varying the duration and temperature of leaching. The leaching conditions considered optimal are as follows.^{5,6}

- 15 ml of 85% H_3PO_4 per gram of Kocite material
- 180°C for 20 hrs.

Such process conditions remove all but about 0.1 wt-% of the aluminum.⁶

At the beginning of the contract period a 5 liter flask apparatus was used for the leaching process. The flask accepted a 175 g Kocite batch charge and produced ~40 g of leached Kocite. This facility was scaled up to accommodate a 12 liter flask allowing the use of a 420 g charge of the standard Hydral 705-based Kocite material. About 100 to 150 g of leached Kocite material were produced per batch.

Figure 4

Nitrogen Desorption Pore Volume
Distributions for Kocite Materials
from hydral 705 Alumina, Kaiser
Substrate Alumina and Alon Alumina

PORE VOLUME DISTRIBUTION

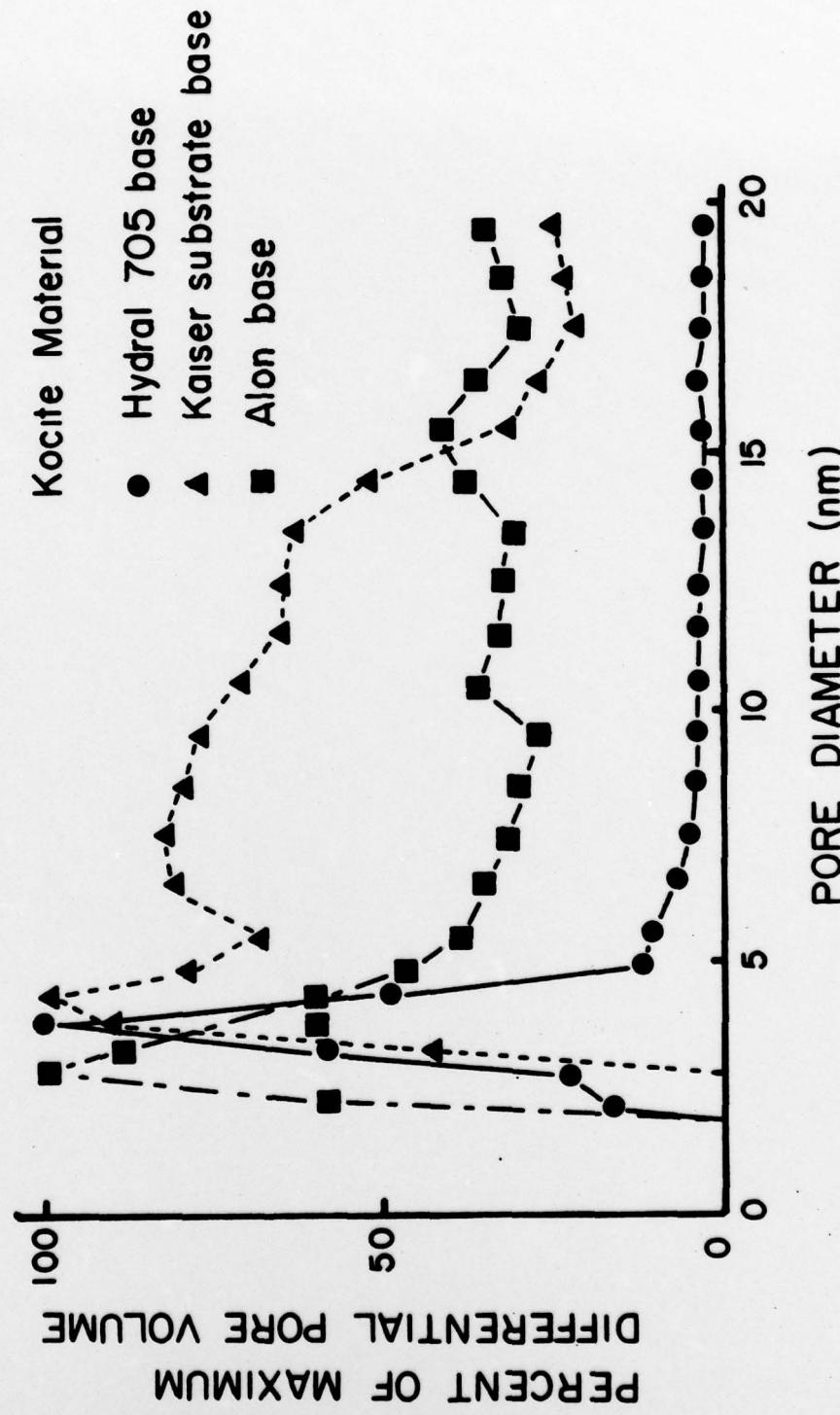


Table V
Characteristics of Kocite^R Materials

<u>Batch Number</u>	3648-9	3648-110	3648-118	3648-139	3648-143	3648-153
<u>Preparation</u>	Hydral 705	Hydral 705	Hydral 705	Alon	Hydral 705	Hydral 705
Substrate	~0.3	~0.3	~0.3	~0.05	~0.3	~0.3
Particle Size (10 ³ nm)	C ₆ H ₆					
Pyropolymer Precursor	850	842	840	900	846	842
Pyrolysis Temperature (°C)						
<u>Characteristics</u>						
Carbon Content (Wt-%)	22.3	21.9	25.3	24.8	27.9	26.6
Resistivity, ρ , @ 25°C (Ω-cm)	0.079	0.12	0.13	0.029	0.093	0.068
Apparent Bulk Density (g/ml)	0.32	0.31	0.32	0.11	0.30	0.32
Surface Area (m ² /g)	63	86	92	102	84	147
Pore Volume (ml/g)	0.09	0.12	0.12	0.18	0.11	0.19
Average Pore Diameter (nm)	5.7	5.6	5.2	7.1	5.2	5.2

The characteristics of the leached Kocite materials used in electrocatalyst preparation during this period are listed in Table VI.^{5,6} Leached Kocite materials are denoted by the addition of an "L" following the Kocite batch identification number. With two exceptions, the leached Kocite materials listed in this table were produced from Hydral 705-based Kocite materials. With this material an approximately 9 fold increase in surface area per gram is obtained by removing the alumina substrate. For the Kaiser and Alon-based Kocite materials the increase in surface area is less dramatic, the leached Kaiser-based material having a 6.5 fold increase to 386 m²/g and the leached Alon-based material having a 4.5 fold increase to 267 m²/g. The different surface area increases for the various types of leached material reflect the differing carbon content and pore structure of the starting Kocite materials.

For each type of leached Kocite material a pore volume distribution is shown in Figures 5, 6 and 7 and compared with the PVD's of the starting Kocite materials. As shown in Figure 5, the pore sizes for the Hydral 705-based Kocite material increase after leaching but remain sharply peaked with the PVD peak moving from ~4.0 to ~6.0 nm. In the case of the Kaiser-based material the PVD remains broad after leaching, although it is somewhat narrower with most of the pores having diameters less than 10 nm as shown in Figure 6. The Alon-based material shows the most dramatic change. As shown in Figure 7, the PVD narrows dramatically and is sharply peaked near 6.0 nm. In particular, the relative volume of pores with diameters larger than 10.0 nm is greatly reduced. A comparison of the PVD's of the three different types of leached material is shown in Figure 8. The PVD's of the leached Hydral 705 and Alon-based Kocite materials are quite similar suggesting that these materials may provide an electrocatalyst support having similar performance characteristics except for a possible reduction in cathode diffusion losses as a result of the substantially smaller particle size and increased particle size uniformity of the leached Alon-based Kocite material.

2.4 Leached Kocite Materials (August, 1978-April, 1979)

The properties of the leached Kocite materials used during this contract period are summarized in Table VII. All but one of these materials, 3648-139L, involves a Hydral 705-based Kocite material. The surface area of this material of 545 m²/g is over twice that of the leached Alon-based Kocite material listed in Table VI, 3648-104L, as a result of the lower carbon content of the starting Kocite material.

Table VI
Leaching Parameters of Kocite^R Materials and Electrocatalysts*

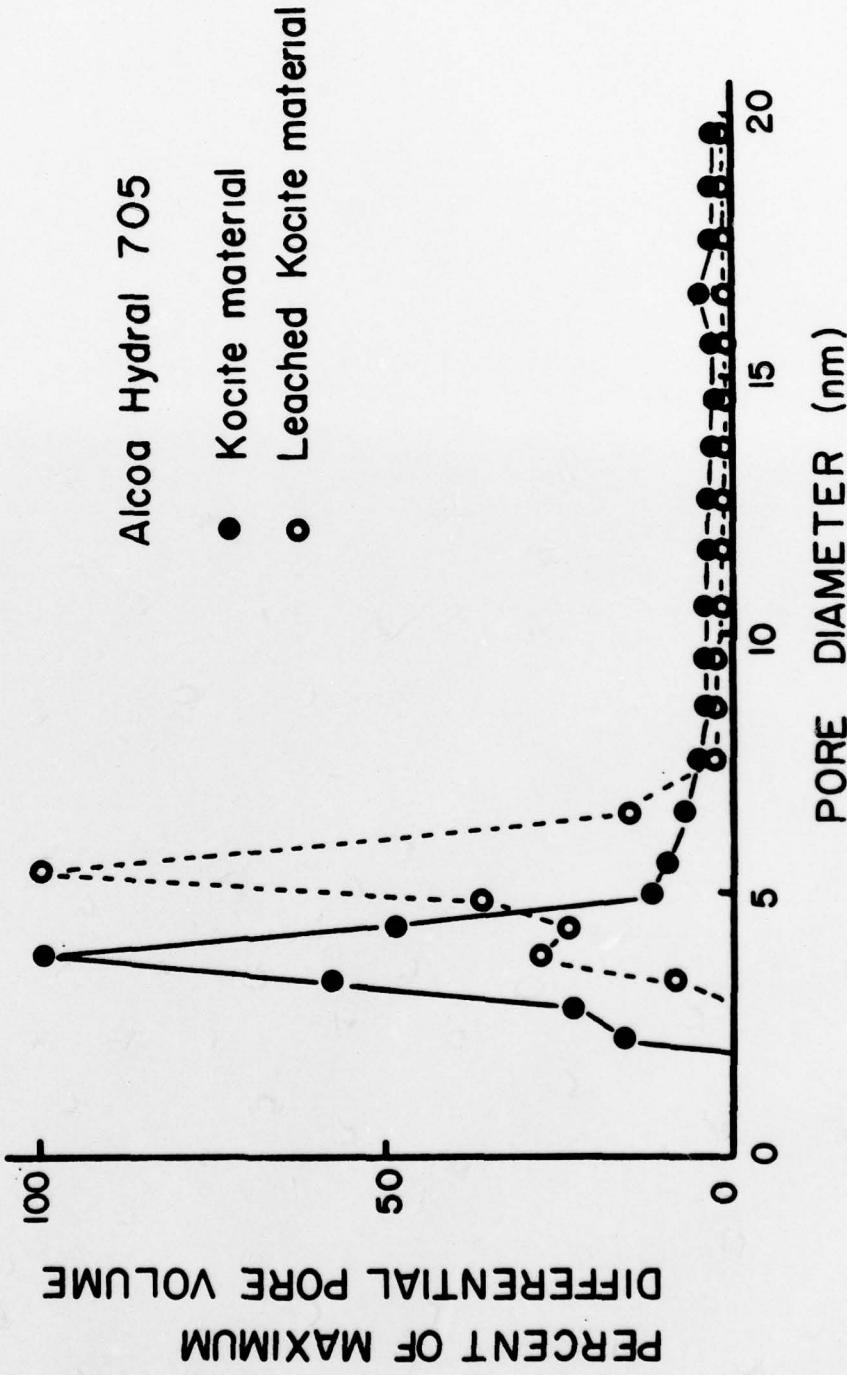
<u>Batch Number</u>	3289-120L	3576-20AL	3576-60L	3648-66L	3648-68L	3648-104L	3380-65L
<u>Preparation</u>							
Kocite Material or Electro-catalyst Batch Used	3289-120	3576-20A	3576-60	3648-66	3648-68	3648-104	3380-65
Leaching Temperature (°C)	140	143	142	179	180	180	181
Leaching Time (Hrs.)	24	24	24	24	20	20	21
<u>Characterization</u>							
Carbon Content (Wt-%)	81.2	69.8	83.6	92.7	92.4	90.3	89.1
Surface Area (m ² /g)	989	619	881	655	645	267	386
Pore Volume (ml/g)	1.76	1.11	1.57	1.29	1.17	0.59	0.90
Average Pore Diameter (nm)	7.1	7.2	7.1	7.9	7.3	8.8	9.3

*See references 5 and 6.

Figure 5

Nitrogen Desorption Pore Volume
Distribution for Hydral 705 Based Kocite
and Leached Kocite Materials

PORE VOLUME DISTRIBUTION



PORE VOLUME DISTRIBUTION

Figure 6

Nitrogen Desorption Pore Volume
Distribution for Kaiser Based Kocite
and Leached Kocite Materials

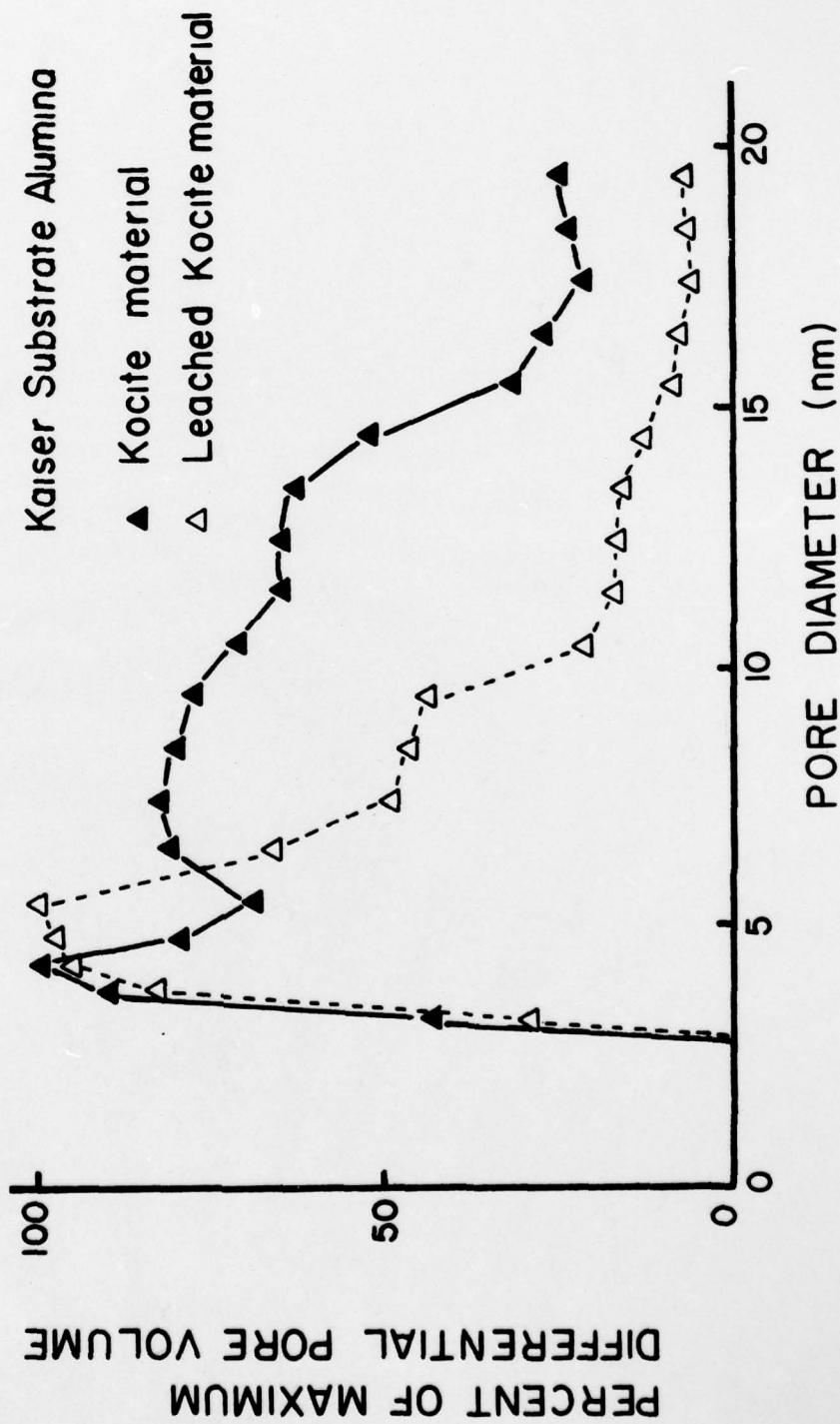
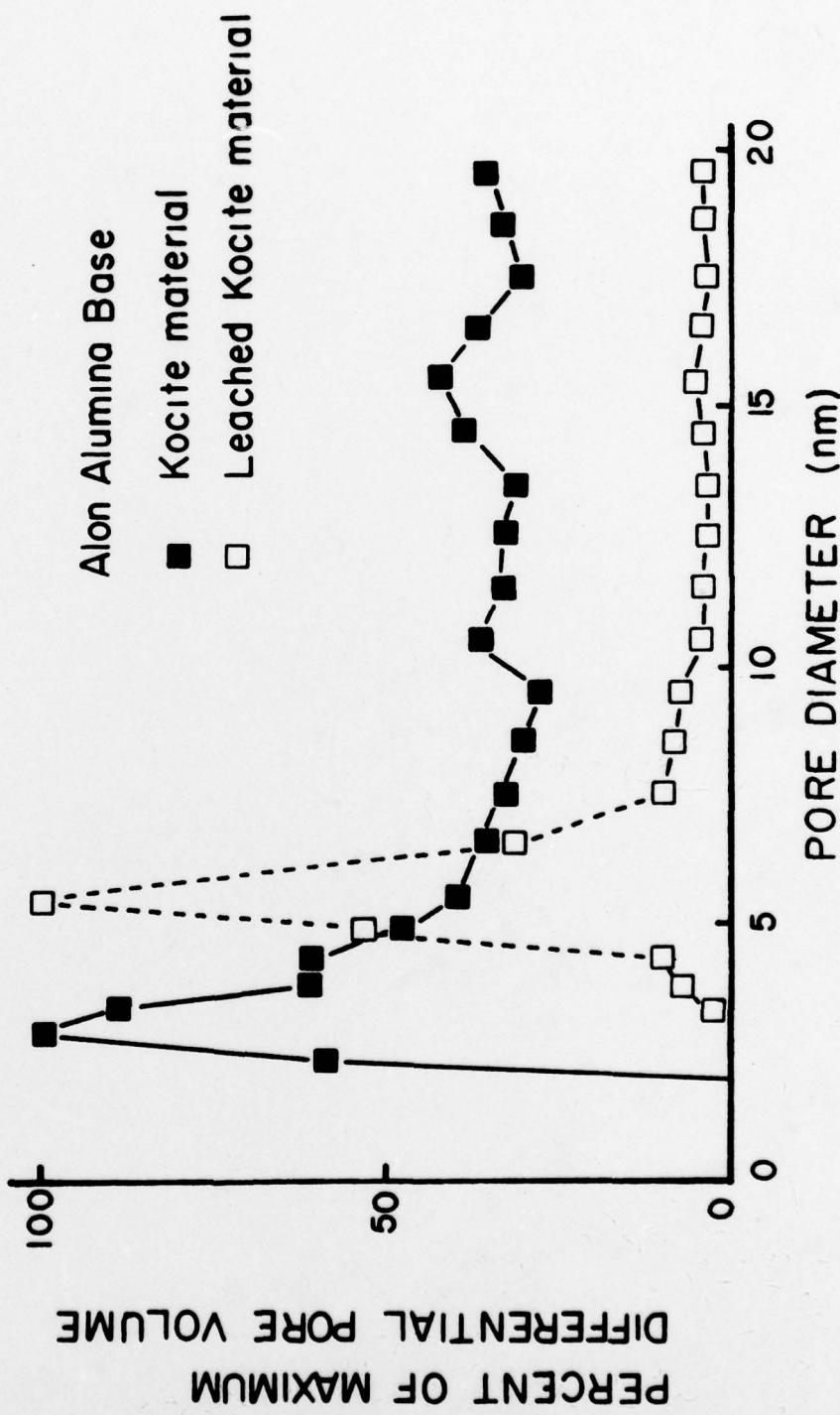


Figure 7

Nitrogen Desorption Pore Volume
Distribution for Alon Based Kocite
and Leached Kocite Materials

PORE VOLUME DISTRIBUTION



Nitrogen Desorption Pore Volume Distribution for Leached Kocite Materials from Hydral 705 Alumina, Kaiser Substrate Alumina and Alon Alumina

PORE VOLUME DISTRIBUTION

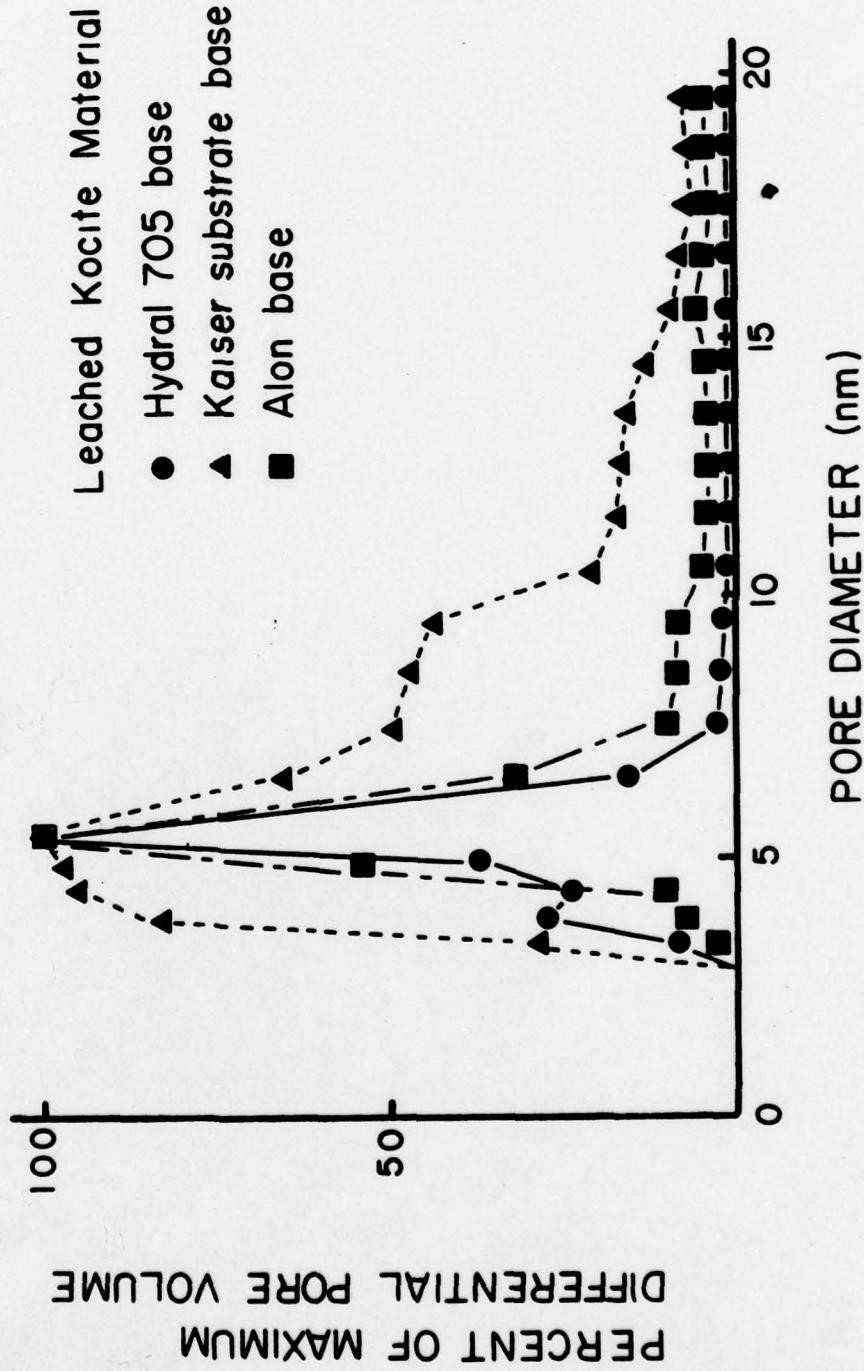


Table VII
Leaching Parameters of Kocite^R Materials

<u>Batch Number</u>	3648-9L	3648-110L	3648-115L	3643-118L	3648-139L	3648-143L	3648-153L
<u>Preparation</u>							
Kocite Material Used	3648-9	3648-110	Combined 3648-9L & 3648-110L	3648-118	3648-139	3648-143	3648-153
<u>Leaching Temperature (°C)</u>							
Leaching Temperature (°C)	181	180		180	181	180	179
Leaching Time (Hrs)	20	20		20	20	20	20
<u>Characterization</u>							
Carbon Content (Wt-%)	96.2	91.7		90.8	84.6	92.0	91.1
Surface Area (m ² /g)	635	785		815	545	804	803
Pore Volume (ml/g)	1.14	1.46		1.45	1.42	1.42	1.33
Average Pore Diameter (nm)	7.2	7.4		7.1	10.4	7.1	6.6

III. KOCITE-DERIVED ELECTROCATALYSTS

3.1 Kocite-Derived Electrocatalyst Preparations (September, 1975-August, 1978)

At the inception of the contract, Kocite-derived electrocatalysts were prepared in small quantities of 5 to 30 grams of unleached electrocatalyst material.² As the need for larger electrocatalyst batches became more apparent, the various process steps were scaled up in size to accommodate electrocatalyst batches of 50 to 150 grams using leached Kocite support materials.^{5,6} The preparation details and physical properties of important Kocite-derived electrocatalysts evaluated during this period²⁻⁶ are listed in Table VIII. For most of the electrocatalysts the platinum source was chloroplatinic acid (CPA). A number of other impregnation sources were tried, such as platinum acetylacetone and sodium platinate, but with less success than the techniques listed in Table VIII. The thiomalic acid/CPA mixture gave good results on one electrocatalyst batch but the results were not repeatable and this approach was abandoned. Also indicated in this table is whether the platinum was impregnated into the Kocite or leached Kocite material. Electrocatalysts to the left of batch 3239-127A in Table VIII were not leached prior to incorporation into electrodes, while the remaining and more recently prepared materials were leached and then made into electrodes. The surface area of these latter electrocatalysts was typically in excess of 600 m²/g.

To determine the effectiveness of each impregnation technique in achieving a high Pt dispersion, X-ray linewidth analyses of the platinum crystallite size were performed. The results of these analyses are also given in Table VIII. The percentage of Pt particles having diameters between \sim 2.0 and 100 nm were determined, as well as the average diameter of Pt particles in this size range when the X-ray data are compared against those of a standard.² The numbers listed under agglomeration give the fraction of the Pt atoms in Pt particles with a diameter greater than \sim 20 Å. Smaller Pt particles did not make a measurable contribution to the Pt X-ray linewidth.

Based on the X-ray linewidth determination of the Pt dispersion, three conclusions can be stated:

- A. A high Pt dispersion on high-surface-area leached Kocite supports is more difficult to achieve with Pt sources such as CPA and PDD than on unleached Kocite supports. However, the electrocatalysts must be leached prior to electrode manufacture.
- B. Leaching the Kocite material prior to Pt impregnation results in a higher Pt dispersion than by impregnation of a Kocite material and subsequently leaching the electrocatalyst.

Table VIII
Platinum Impregnation of Kocite^R Materials

Batch Number	3289-25F	3380-125B	3380-156G	3289-127A	3576-20AL	3576-61A
<u>Preparation</u>						
Kocite Material Used	3289-25	3380-125	3380-156	3289-120L	3576-20	3576-60L
Platinum Source ^a	thiomalic acid/CPA	CPA	CPA	CPA	CPA	PDD
Solvent	H ₂ O	H ₂ O/C ₂ H ₅ OH		H ₂ O/C ₂ H ₅ OH	H ₂ O/C ₂ H ₅ OH	H ₂ O
Reduction Atmosphere	H ₂	H ₂		H ₂	H ₂	H ₂
Reduction Temperature (°C)	260	260	260	260	260	260
<u>Characteristics</u>						
Batch Size (g)	25	30	220	60	60	10
Platinum Concentration, (wt-%)	9.8	4.9	10	17.3	14.9	11.4
Surface Area (m ² /g)			80	661	619	620
Pore Volume (ml/g)				0.11	1.11	1.07
Average Pore Diameter (nm)				5.5	7.2	6.9
Pt Addition	To Kocite	To Kocite	To Kocite	To Leached Kocite	To Kocite	To Leached Kocite
Pt Agglomeration ^b (%)	30	12	22	37	57	9
Pt Crystallite Size ^c (nm)	3.4	4.4	6.6	6.7	9.2	4.7

^aCPA = chloroplatinic acid, PDD = platinum diaminedinitrite.

^bDetermined by comparison with a fully agglomerated electrocatalyst standard.

^cMean size of crystallites over \sim 2.0 nm diameter.

Table VIII (Cont'd)
Platinum Impregnation of Kocite R Materials

<u>Batch Number</u>	3576-61B	3648-66A	3648-68A	3648-94A
<u>Preparation</u>				
Kocite Material Used	3576-60L	3648-66L	3648-68L	3648
Platinum Source ^a	CPA	CPA	CPA	-66A and -68A
Solvent	H ₂ O	H ₂ O	H ₂ O	
Reduction Atmosphere	H ₂	H ₂	H ₂	
Reduction Temperature (°C)	260	260	260	
<u>Characteristics</u>				
Batch Size (g)	10	105	113	118
Platinum Concentration, (wt-%)	16.3	15.7	15.8	15.5
Surface Area (m ² /g)	604	625	597	
Pore Volume (ml/g)	1.29	1.22	1.19	
Average Pore Diameter (nm)	8.5	7.8	8.0	
Pt Addition	To Leached Kocite	To Leached Kocite	To Leached Kocite	To Leached Kocite
Pt Agglomeration ^b (%)	25			34
Pt Crystallite Size ^c (nm)	5.2	5.0		

^a CPA = chloroplatinic acid, PDD = platinum diamminedinitrite.

^b Determined by comparison with a fully agglomerated electrocatalyst standard.

^c Mean size of crystallites over ~2.0 nm diameter.

C. Using PDD as the Pt source generally results in a higher Pt dispersion than the use of CPA.

3.2 Kocite-Derived Electrocatalyst Structure

The particle shape, platinum particle size, platinum particle distribution, and pore volume distribution of several Kocite-derived electrocatalysts were characterized by PVD and TEM studies. Within experimental error, the PVD of a leached Kocite material and the resulting electrocatalyst are identical. As a result no PVD results on electrocatalysts will be reported.

TEM studies⁷ made on several Kocite-derived electrocatalysts prepared by CPA impregnation techniques indicate that the features elucidated by this technique are quite similar from electrocatalyst to electrocatalyst. The most important conclusions can be summarized by referring to Figures 9 and 10, TEM's which are typical of electrocatalysts as currently produced. In Figure 9, both the platinum particles (dark spots) and the porous nature of an electrocatalyst particle are clearly visible. Of particular interest in this figure are the distribution and size of the platinum particles. While the platinum dispersion is good over most of this particle, the area in the upper left hand corner contains a number of large (>10 nm dia) platinum particles. The existence of these large platinum particles clearly indicates this platinum impregnation technique results in a bimodal Pt size distribution and is not optimized. It also implies that improved fuel cell performance should be attainable when a more uniform, more highly dispersed platinum distribution can be produced.

The porosity and pore structure of Kocite-derived electrocatalyst particles are clearly demonstrated in the TEM of Figure 10. The diameter of the pores shown in this figure are mostly in the 5.0-10.0 nm range, consistent with the PVD results in Figures 4 and 8. While platinum particle placement on the leached Kocite support is difficult to determine from Figures 9 and 10, it is believed that higher resolution TEM data could provide useful information in this area.

3.3 Kocite-Derived Electrocatalyst Preparations (August, 1978-April, 1979)

The electrocatalyst preparations which were evaluated during the most recent contract period are listed in Table IX. The 3648-115C electrocatalyst was the first large batch prepared successfully using PDD as the Pt source. This batch has a substantially higher Pt dispersion than large batches prepared during earlier contract periods. A typical TEM of electrocatalyst particles of this batch is shown in Figure 11. In general, the Pt distribution shown in Figure 11 is more uniform than that of Figure 9 although numerous larger Pt particles are still evident. The particles shown in this figure appear to have a

Figure 9

Transmission Electron Micrograph of
Electrocatalyst 3648-94A

25 nm



Figure 10

Transmission Electron Micrograph of
Electrocatalyst 3648-94A

25 nm

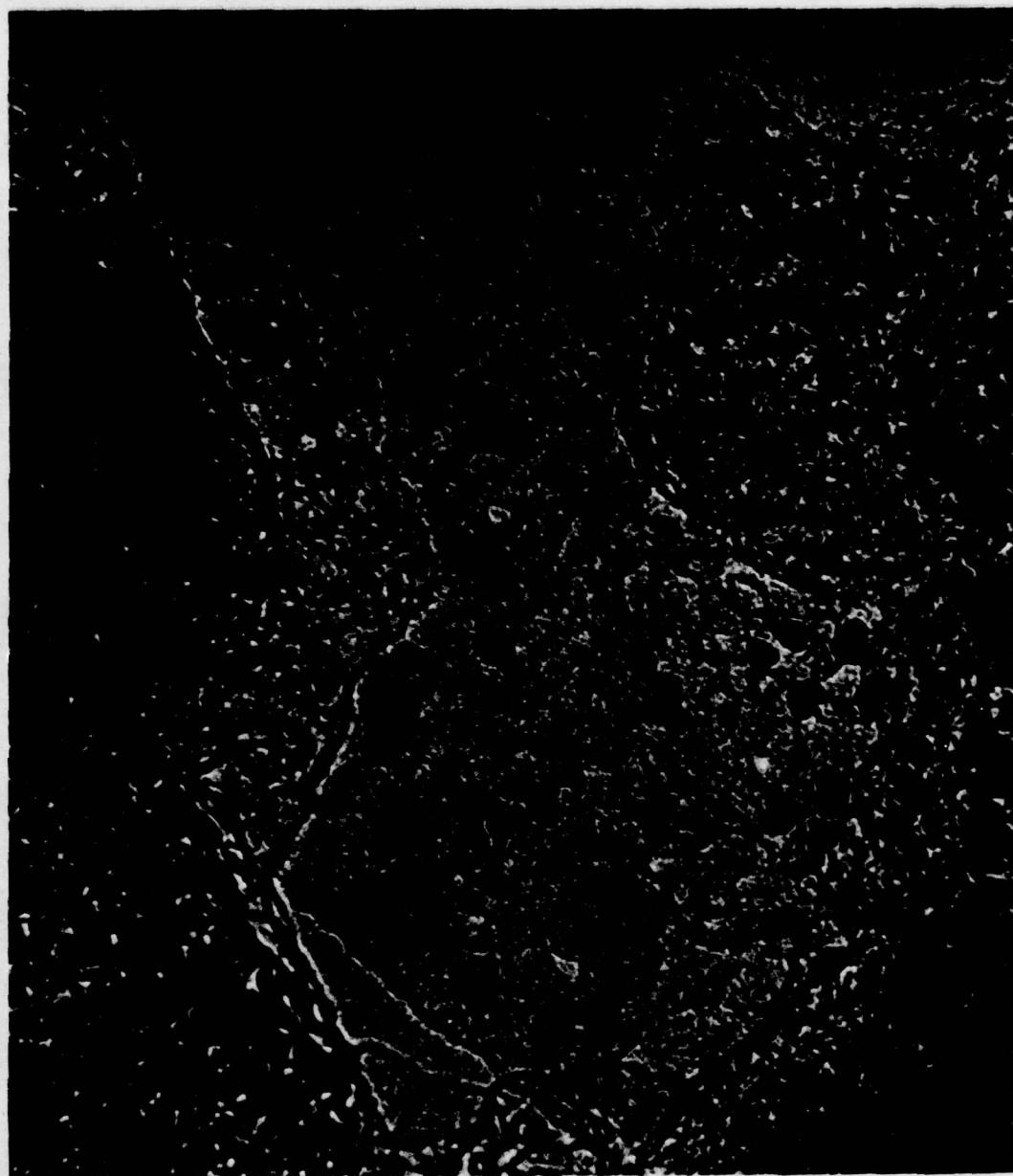


Table IX
Platinum Impregnation of Kocite^R Materials

<u>Batch Number</u>	3648-115C	3648-118A	3648-139A	3648-143A	3648-153A
<u>Preparation</u>					
Kocite Material Used	3648-115L	3648-118L	3648-139L	3648-143L	3648-153L
Platinum Source ^a	PDD	CPA	CPA	PDD	PDD
Solvent	1.0 M HNO ₃	H ₂ O	H ₂ O	1.0 M HNO ₃	1.0 M HNO ₃
Reduction Atmosphere	H ₂	H ₂	H ₂	H ₂	H ₂
Reduction Temperature (°C)	260	260	260	257	260
<u>Characteristics</u>					
Batch Size (g)	53	51	65	105	52
Platinum Concentration, (Wt-%)	14.6	11	13.6	14.6	15.1
Surface Area (m ² /g)	624	709	530	694	692
Pore Volume (ml/g)	1.09	1.24	1.24	1.09	1.09
Average Pore Diameter (nm)	7.0	7.0	9.4	6.3	6.3
Pt Agglomeration ^b (%)	17	16	28	23	10
Pt Crystallite Size ^c (nm)	3.8	4.2	4.1	6.0	4.2

^aCPA = chloroplatinic acid, PDD = platinum diaminedinitrite.

^bDetermined by comparison with a fully agglomerated electrocatalyst standard.

^cMean size of crystallites over ~2.0 nm diameter.

Figure 11

Transmission Electron Micrograph of
Electrocatalyst 3648-115C

25 nm



particularly heavy Pt loading indicating the particle to particle Pt distribution is still non-uniform and that improved impregnation techniques should result in higher Pt dispersions and presumably a more sinter resistant electrocatalyst.

The 3648-118C electrocatalyst batch was prepared at ~10 wt-% Pt instead of the usual 15 wt-% Pt to allow a thicker electrode catalyst layer to be prepared while maintaining the normal electrode Pt loading.

Electrocatalyst batch 3648-139A, using a leached Alon-based Kocite material was prepared to determine how this type of electrocatalyst would perform relative to standard electrocatalyst batches such as 3648-94A and 115C. A typical TEM of particles from this batch is shown in Figure 12. A bimodal Pt distribution on these particles is evident.

Two electrocatalyst batches were both prepared using PDD. Batch 3648-143A is a repeat of batch 3648-115C while batch 3648-153A was oxidized in 2 M HNO₃ for 20 hours prior to Pt impregnation to create more impregnation sites. As determined by the X-ray linewidth analyses, electrocatalyst batch 3648-153A has the highest Pt dispersion of any large Kocite-derived electrocatalyst batch made using a leached Kocite material and would be expected to have the best performance in an electrode of any batch prepared during this program. Two pictures of the 3648-153A electrocatalyst batch are shown in Figures 13 and 14. In Figure 13, a good Pt dispersion is evident although occasional larger Pt particles can be seen. In Figure 14, the Pt dispersion appears to be substantially better. A comparison of these figures again indicates that a further improvement of the Pt distribution among the leached Kocite particles is desirable.

Figure 12

Transmission Electron Micrograph of
Electrocatalyst 3648-139A

25 nm



Figure 13

Transmission Electron Micrograph of
Electrocatalyst 3648-153A

25 nm

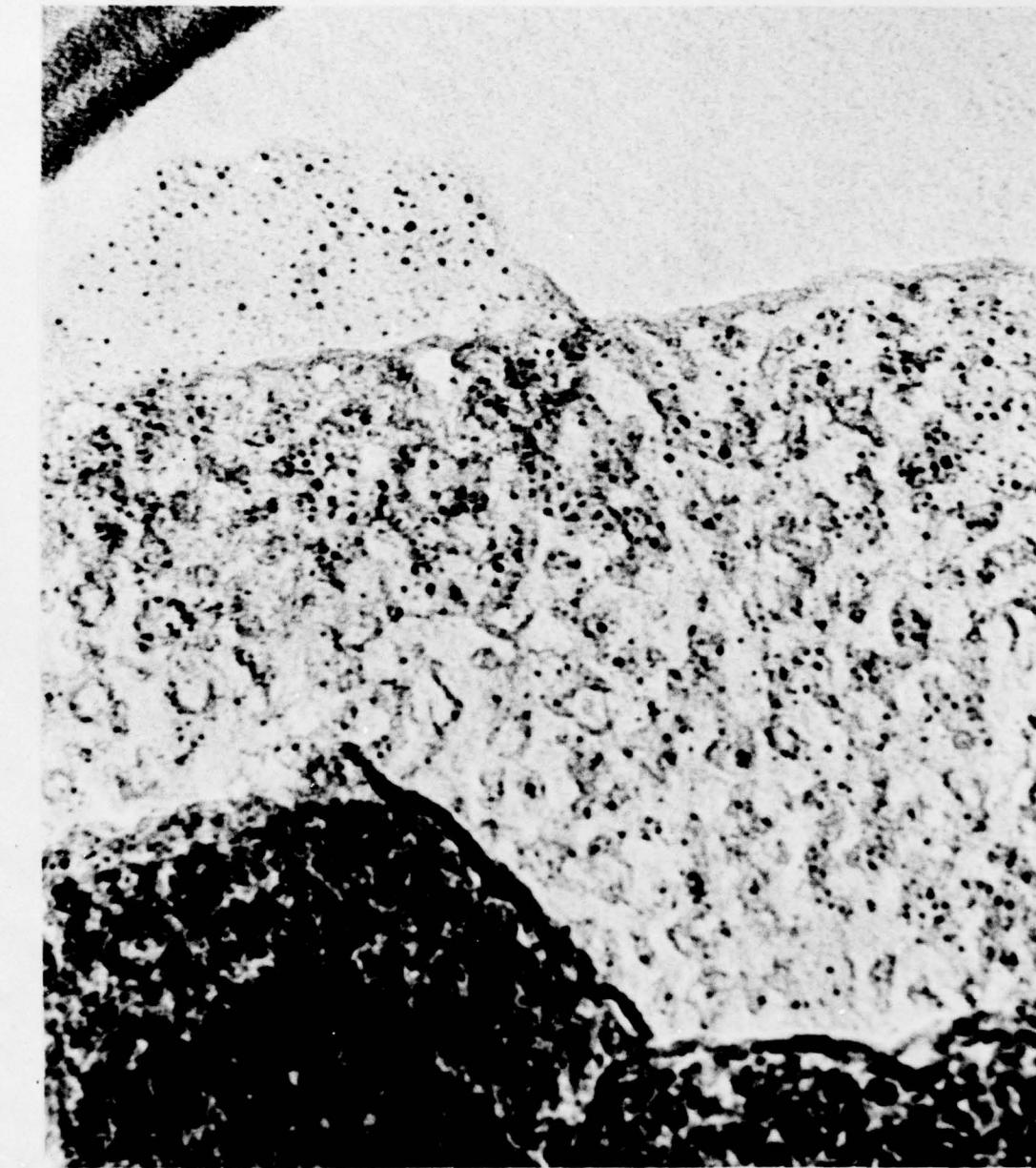
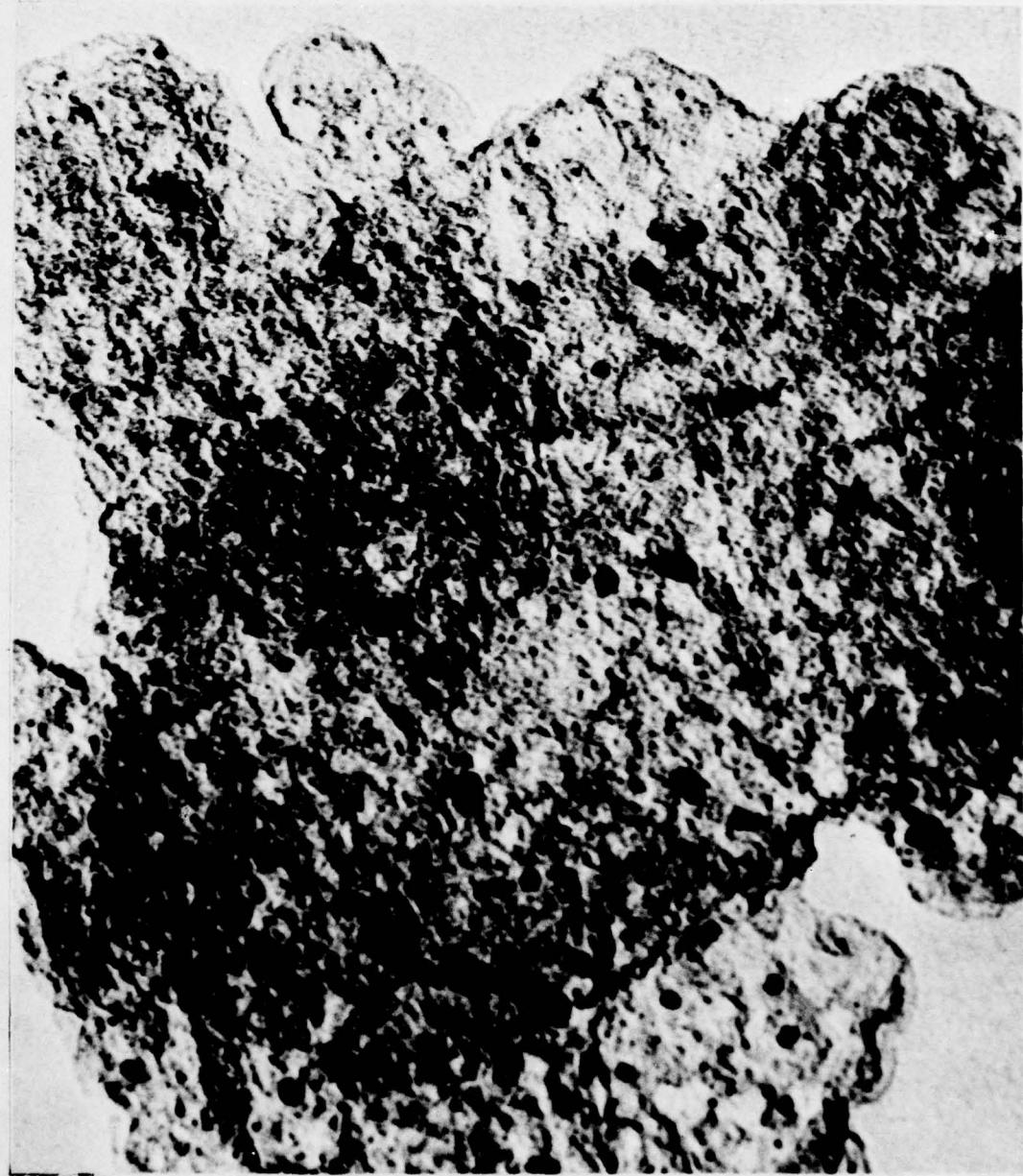


Figure 14

Transmission Electron Micrograph of
Electrocatalyst 3648-153A

25 nm



IV. KOCITE ELECTRODE FABRICATION AND TESTING

4.1 Electrode Fabrication

Two different electrode fabrication processes were utilized by ERC during this program. The first process is a standard electrode fabrication technique and involves use of a machine calendering mill. The second process is more of an experimental technique and can be described as a sheet mold process.

The fuel cell electrodes prepared under this contract consisted of two parts, a catalyst layer and an electrode substrate. The catalyst layer, consisting of the electrocatalyst and a binder, was mounted on the substrate which served as a current collector as well as a gas diffusion path. The electrode substrate was a highly porous and conductive carbon fiber paper such as produced by Stackpole Carbon Co. The substrate was wetproofed with FEP, a copolymer of tetrafluoroethylene and hexafluoropropylene, to prevent electrolyte entrapment within its pores. The FEP content of the electrode backing was generally in the range of 35 to 40 percent.

A discrete catalyst layer was produced during the machine calendering process. This process initially consists of wet blending the electrocatalyst with a dry PTFE powder and a filler using a petroleum distillate type of medium. The filler, a decomposable material such as ammonium bicarbonate served to aid in ease of handling during the rolling operation. After allowing the solvent to evaporate over a period of several days, the filler could be removed by gentle heating.

The rolling technique utilized throughout the contract essentially remained the same. The catalyst layers produced by the rolling process were eventually laminated to the electrode substrate. During the last year of the program the pressure to bond the layer to the carbon paper was increased to 300 psi. This was done to ensure adequate adhesion between the two components and prevent any electrolyte entrapment between the catalyst layer and electrode backing.

The sheet mold process did not involve the production of a discrete catalyst layer. The layer instead was formed by directly placing a catalyst - PTFE mixture onto the electrode substrate. Electrodes produced by either technique were subsequently sintered at 350°C for a period of 20 minutes. The sintering operation gave a hydrophobic nature to the catalyst layer to insure ready reactant access to the electrocatalyst.

The thickness of a final electrode would be dependent upon the Pt content of the catalyst as well as the Pt loading of the electrode. For a typical catalyst batch of 15% Pt, and a typical electrode loading

of 0.6 mg/cm^2 Pt, the catalyst layer averaged about 0.005" thick. Since the electrode substrate remained constant at about 0.018" thick, the typical total electrode thickness was 0.023".

4.2 Cell Assembly and Test Procedures

The evaluation of test electrodes prepared from Kocite-derived electrocatalysts was performed under test conditions which closely simulate electrode behavior in a fuel cell system. Although the cell size was maintained at 25 cm^2 , the electrodes were tested in conjunction with other low cost components which are projected to be viable for an actual fuel cell. The other components include Kynol matrices, carbon fiber electrode substrates and molded graphite cell plates. These cell components are shown in Figure 15.

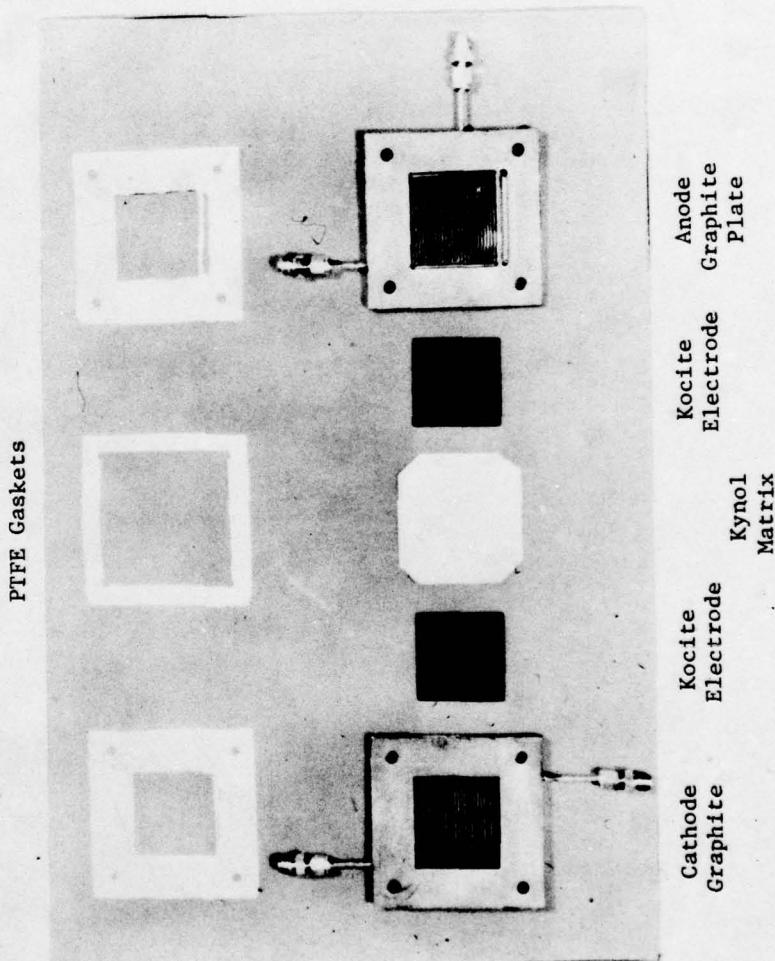
The Kynol matrix, a composite structure of Kynol fibers and a phenolic binder was used in the vast majority of test cells. The matrix which physically separated the anode from the cathode also serves as a barrier to prevent cross mixing of reactant gases. The Kynol matrices, as produced by a conventional paper making process, averaged about 0.018 inches in thickness. A few cells early in the program contained an experimental fibrous type SiC matrix. Although the results were very encouraging with the experimental matrix, this approach was subsequently terminated due to availability problems with the SiC. During the last year of this study, ERC believed that the ability of a Kocite electrode to reach a high performance level was not being hindered in any way by the cell matrix.

Cells during this program were constructed in molded graphite hardware except for the first few cells in 1975 which contained tantalum plates. The graphite plates were a composite structure of a commercially available graphite and an acid resistant resin. The plate on the hydrogen side of the cell also contained a slot which served as a reservoir to periodically replenish acid to the cell components.

Emphasis during cell testing was generally placed upon the evaluation of Kocite electrodes as cathodes for oxygen electroreduction of either air or oxygen. Prior to two years ago, evaluation of Kocite cathodes did present some complications for ERC not normally experienced with other types of fuel cell electrodes. It was necessary to prefill the Kocite electrode by a float fill process in order to maximize performance. At the same time, the experimental cathode had to be tested versus a 2 mg/cm^2 Pt black anode because of relatively poor stability exhibited by Kocite anodes. These abnormalities were later shown to be related to the fact that the alumina portion of the catalyst support

Figure 15

Fuel Cell Test Hardware



could be attacked by phosphoric acid during cell operation. Cells containing Kocite electrodes were therefore suspected of being electrolyte limited because of the alumina corrosion.

When leached Kocite supports were utilized in the final two years of this program, the difficulties associated with cell assembly were considerably lessened. During the last year it was possible to operate cells stably in which both the anode and cathode contained the identical electrode structure. The optimum cell assembly procedure was to initially saturate the matrix with phosphoric acid and compress it between the two dry electrode structures. The electrodes and matrix were compressed to about 60 percent of the total of their initial thicknesses. Filling of the electrodes with phosphoric acid did occur by the squeezing out of excess electrolyte from the matrix during assembly. Further electrode filling could also occur during cell operation if electrolyte replenishment was made. The cell matrix, in intimate contact with the reservoir, could transport additional electrolyte by a wicking mechanism.

Attempts were made during this program to control the initial acid concentration added to cell components at a value which closely approximates the equilibrium acid concentration existing in a continually operating cell. The equilibrium acid concentration is dependent upon cell operating temperature and the stoichiometric conversion percentage of air in the cell. Since cell operating temperatures increased from 140°C to 180°C during the course of this program, the initial acid concentration also increased. During the last year of this program, the acid was prepared at a concentration between 100 and 102% by initially heating the as-received 85% acid at 180°C for several hours. The equilibrium acid concentration in a cell operating at 180°C and with a three stoichiometric air flow rate is estimated to be about 101.6%. Higher air flow rates would result in further concentration of the acid in the fuel cell.

Test cells were usually operated on pure hydrogen to the anode and either air or oxygen to the cathode. The hydrogen flow was at a minimum purge rate while the air flow prior to the last year of this program was held at the 5 stoichiometric rate. The normal endurance condition was to operate the cell on hydrogen and air at 180°C at 100 ma/cm². During the last year of this study, the endurance parameters were changed to operate cells at 200 ma/cm² and the 3 stoichiometric air flow rate. These more severe operating conditions appeared to have no detrimental effect on the stability of Kocite electrodes, if the electrode structure had no tendency to flood. It was even possible to operate stably if the Kocite electrodes had good gas diffusional characteristics at the 2 stoichiometric rate. A penalty of about 10 mV was suffered, however, due to the drop in oxygen partial pressure.

Throughout the entire program there was continual progress in achieving high initial performance levels with Kocite electrodes. This probably is due to better wetting characteristics of the electrocatalyst and more uniform electrode structures. During the last year, many of the techniques such as cell reversal and electrode pre-polarization which appeared to aid increased performance could be eliminated. Prior to the last year, cells were allowed to sit overnight at the operating temperature before startup to aid in acid distribution within the cell. During the last year, cell startup occurred shortly after assembly as soon as the cell reached about 140°C. This was performed to eliminate any possible corrosion effects that an idle cell may experience at high temperatures.

V. RESULTS AND DISCUSSION

5.1 Introduction

In this section, the characteristics and performance of Kocite electrodes tested at UOP and ERC during this program are discussed. In section 5.2, the results obtained with Kocite electrodes up to January, 1978 are reviewed along with some of the important program milestones. In section 5.3, the results obtained since January, 1978 are presented emphasizing the peak performance achieved during the program, the degree of electrode reproducibility observed, and the results of cell endurance tests. Finally, the results achieved during this program are summarized in section 5.4.

5.2 Cell Performance Results (September, 1975-December, 1977)

The cell performance results recorded during this period are briefly summarized in this section. The Kocite electrodes tested between September, 1975 and February, 1976 were fabricated with unleached Kocite materials and had to be prewetted in H_3PO_4 for the cells to run well. At 100 ma/cm^2 and 140°C , the best performance was obtained with batch 3289-25F which used a Kaiser-based Kocite material. At $\sim 0.5 \text{ mg/cm}^2$ Pt loading, terminal and IR free voltages of 590 and 630 mV, respectively, with oxygen gain figures of $\sim 110 \text{ mV}^2$.

Substantial performance improvements were achieved during the next contract period of February, 1976 to August, 1976. At 149°C and 100 ma/cm^2 , terminal and IR free cell voltages of 580 and 670 mV, respectively, were obtained with lower Pt loaded (0.22 mg/cm^2) electrodes using batch 3380-125B, a Hydral 705-based material.³ Oxygen gain figures were reduced to $\sim 90 \text{ mV}$.

From September, 1976 to December, 1976 the best results were obtained using batch 3380-156G, a Hydral 705-based material. At 100 ma/cm^2 and 180°C , the best cell with a Kynol matrix reached 650 mV terminal voltage with an oxygen gain of 60 mV.⁴ This cell had a 0.42 mg/cm^2 Pt-loaded Kocite electrode. A cell with an experimental SiC matrix reached 660 mV under the same conditions using a 0.54 mg/cm^2 Pt-loaded electrode. The lower oxygen gain figures for this period indicated that substantial improvements were made in the electrode structure.

The cell test results of electrocatalysts prepared from leached Hydral 705-based Kocite materials from March to December, 1977 are summarized in Table X.⁵ These electrodes no longer needed prewetting and the reproducibility of cell performance improved substantially. Cells were tested routinely at both 100 and 200 ma/cm^2 . A cell, with a 0.6 mg/cm^2 Pt-loaded sheet mold electrode using batch 3576-61B, reached

Table X

Characteristics and Performance of Pt-Doped Kocite Electrodes^a

- March 1977 to December 1977 -

Electrode Characteristics

Cell Build Number	Kocite Electrocatalyst Batch	Platinum Loading (mg/cm ²)	PTFE Content (Wt-%)	Fabrication Method	Electrode Prewetting (days)
ERC-113	3289-127A	0.55	50	Machine Rolled	1
ERC-132	3576-61B	0.56	40	Sheet Mold	0.1
ERC-138	3576-61B	0.60	40	Sheet Mold	None
ERC-140 ^b	3576-61B	0.60	40	Sheet Mold	None

Electrode Performance at 180°C

Cell Build Number	Kocite Electrocatalyst Batch	@ 100 mA/cm ²		Terminal Voltage (mV) @ 200 mA/cm ²	Oxygen
		Air	Oxygen		
ERC-113	3289-127A	670	725	600	665
ERC-132	3576-61B	670	730	600	670
ERC-138	3576-61B	680	740	620	685
ERC-140 ^b	3576-61B	670	730	600	670

^aReference

^bExcept for cell ERC-140, having a Kocite anode and cathode, 2 mg/cm² Pt-black counter electrodes were used.

620 mV at 200 ma/cm² with an oxygen gain of 65 mV.⁵ These increased performance levels demonstrated that leaching the Kocite material resulted in a substantially improved electrocatalyst. Endurance testing of cells was typically limited to 1000 hr., but a cell with electrocatalyst 3289-127A was tested for 4300 hrs. During this time the cell reached a peak of 600 mV at 200 ma/cm² and at the 4300 hr. point was operating at 580 mV at the same current.

5.3 Cell Performance Results (January, 1978-April, 1979)

While good performance levels were reached prior to this period and the stability of Kocite-derived electrocatalysts appeared to be very good, the reproducibility of cell performance from cell to cell was not satisfactory.⁵ Using Kocite electrodes from the same electrode batch, cell to cell performance levels often varied by more than 200 mV without obvious cell defects such as gas crossover or electrode misalignment. As a result, the main emphasis during this last program period was on improving the reproducibility of cell performance, particularly for cells with Kocite electrodes from the same electrode batch (i.e. prepared by ERC at the same time). Such a goal required larger electrocatalyst batches. Typically, four 5'x15" electrode sheets (numbered separately) were fabricated at a time to obtain enough 25 cm² electrodes for careful electrode evaluation. Normally, several different electrode batches were prepared and evaluated from the electrocatalyst batches prepared during this period.

The characteristics of Kocite electrodes used during this period are listed in Table XI. In this table cells are listed by the electrocatalyst batch in the Kocite electrode. The performance of these cells is listed in Table XII by first electrocatalyst number and then electrode sheet number (sequentially numbered electrode sheets constitute a single electrode batch).

Initially, electrodes were fabricated from electrocatalyst batch 3648-94A using the same techniques and PTFE contents used prior to this period for the best performing electrodes.⁵ As indicated in Table X, the sheet mold technique and a 40 wt-% PTFE had given the best results previously. However, when used with batch 3648-94A, the same techniques produced electrodes which flooded soon after startup and had poor performance levels. As a result, the machine rolling technique was reinstated and a 45 or 50 wt-% PTFE catalyst layer content used. Improved performance was achieved as indicated by the cell data obtained using the 5400-5403 series electrodes. The average cell performance of this series on air at 200 ma/cm² and 180°C was 570 mV terminal with a standard deviation of 31 mV. The spread in cell performance was from 510 to 644 mV for the 17 cells assembled from these electrodes. While not very satisfactory, this performance was a substantial improvement over cell performance reproducibility obtained earlier in the program.

Table XI
Kocite Electrode Characteristics

Cell Number	Kocite-Derived Electrocatalyst Batch	Platinum Content (wt-%)	ERC Electrode Number	Nominal Platinum Loading (mg/cm ²)	PTFE Content (wt-%)	Fabrication Method	
						Sheet	Mold
ERC 160	3648-94A	14.9	4912	~0.60	40		
ERC 161	3848-94A	14.9	4912	~0.60	40	Sheet	Mold
ERC 162	3648-94A	14.9	4914	~0.60	40	Sheet	Mold
ERC 163	3648-94A	14.9	4914	~0.60	40	Sheet	Mold
ERC 164	3648-94A	14.9	4914	~0.60	40	Sheet	Mold
ERC 165	3648-94A	14.9	4912	~0.50	40	Sheet	Mold
ERC 166	3648-94A	14.9	5049	~0.60	40	Sheet	Mold
ERC 167	3648-94A	14.9	5050	~0.60	40	Sheet	Mold
ERC 169	3648-94A	14.9	4573	~0.55	45	Sheet	Mold
ERC 170	3648-94A	14.9	4574	~0.55	45	Sheet	Mold
ERC 171	3648-94A	14.9	4573	~0.55	45	Sheet	Mold
ERC 172	3648-94A	14.9	5400	~0.60	45	Machine	Rolled
ERC 173	3648-94A	14.9	5403	~0.65	45	Machine	Rolled
ERC 174	3648-94A	14.9	4921	~0.55	45	Sheet	Mold
ERC 175	3648-94A	14.9	4921	~0.55	45	Sheet	Mold
ERC 176	3648-94A	14.9	5401	~0.65	45	Machine	Rolled
ERC 177	3648-94A	14.9	5047	~0.60	45	Sheet	Mold
ERC 178	3648-94A	14.9	5401	~0.65	45	Machine	Rolled
ERC 179	3648-94A	14.9	5400	~0.50	45	Machine	Rolled
ERC 180	3648-94A	14.9	5400	~0.60	45	Machine	Rolled
ERC 181	3648-94A	14.9	5400	~0.60	45	Machine	Rolled
ERC 182	3648-94A	14.9	5400	~0.60	45	Machine	Rolled
ERC 183	3648-94A	14.9	5401	~0.65	45	Machine	Rolled
ERC 184	3648-94A	14.9	5401	~0.65	45	Machine	Rolled

Table XI (Cont'd)
Kocite Electrode Characteristics

Cell Number	Kocite-Derived Electrocatalyst Batch	Platinum Content (wt-%)	ERC Electrode Number	Nominal Platinum Loading (mg/cm ²)	PTFE Content (wt-%)	Fabrication Method
UOP	3648-94A-1	14.9	5402	0.58	45	Machine Rolled
UOP	3648-94A-2	14.9	5402	0.58	45	Machine Rolled
UOP	3648-94A-3	14.9	5402	0.58	45	Machine Rolled
UOP	3648-94A-4	14.9	5402	~0.58	45	Machine Rolled
UOP	3648-94A-5	14.9	5403	~0.60	45	Machine Rolled
UOP	3648-94A-6	14.9	5403	~0.60	45	Machine Rolled
ERC 185	3648-94A	14.9	5843	~0.60	45	Machine Rolled
ERC 186	3648-94A	14.9	5846	~0.65	45	Machine Rolled
ERC 187	3648-94A	14.9	5843	~0.65	45	Machine Rolled
ERC 188	3648-94A	14.9	5845	~0.65	45	Machine Rolled
ERC 189	3648-115C	16.8	6047	~0.65	45	Machine Rolled
ERC 190	3648-115C	16.8	6047	~0.65	45	Machine Rolled
ERC 191	3648-115C	16.8	6046	~0.60	45	Machine Rolled
ERC 194	3648-115C	16.8	6048	~0.60	45	Machine Rolled
ERC 195	3648-115C	16.8	6046	~0.60	45	Machine Rolled
ERC 196	3648-115C	16.8	6047	~0.65	45	Machine Rolled
ERC 197	3648-115C	16.8	6047	~0.65	45	Machine Rolled
ERC 198	3648-115C	16.8	6693	~0.60	45	Machine Rolled
ERC 199	3648-115C	16.8	6692	~0.65	45	Machine Rolled
ERC 200	3648-115C	16.8	6692	~0.65	45	Machine Rolled
ERC 201	3648-115C	16.8	6694	~0.65	45	Machine Rolled

Table XI (Cont'd.)
Kocite Electrode Characteristics

Cell Number	Kocite-Derived Electrocatalyst Batch	Platinum Content (wt-%)	ERC Electrode Number	Nominal	PTFE Content (wt-%)	Fabrication Method
				Platinum Loading (mg/cm ²)		
UOP	3648-115C-1	16.8	6048	~0.60	45	Machine Rolled
UOP	3648-115C-2	16.8	6048	~0.60	45	Machine Rolled
UOP	3648-115C-3	16.8	6048	~0.60	45	Machine Rolled
UOP	3648-115C-4	16.8	6048	~0.60	45	Machine Rolled
UOP	3648-115C-5	16.8	6048	~0.60	45	Machine Rolled
UOP	3648-115C-6	16.8	6048	~0.60	45	Machine Rolled
UOP	3648-115C-7	16.8	6045	~0.65	45	Machine Rolled
UOP	3648-115C-8	16.8	6045	~0.65	45	Machine Rolled
UOP	3648-115C-9	16.8	6045	~0.65	45	Machine Rolled
UOP	3648-115C-10	16.8	6045	~0.65	45	Machine Rolled
UOP	3648-115C-11	16.8	6045	~0.65	45	Machine Rolled
UOP	3648-115C-12	16.8	6045	~0.65	45	Machine Rolled
ERC 192	3648-118A	10.0	6043	~0.65	45	Machine Rolled
ERC 193	3648-118A	10.0	6043	~0.65	45	Machine Rolled
UOP	3648-118A-1	10.0	6042	~0.65	45	Machine Rolled
UOP	3648-118A-2	10.0	6042	~0.65	45	Machine Rolled
UOP	3648-118A-3	10.0	6042	~0.65	45	Machine Rolled
UOP	3648-118A-4	10.0	6042	~0.65	45	Machine Rolled

Table XI (Cont'd.)
Kocite Electrode Characteristics

Cell Number	Kocite-Derived Electrocatalyst Batch	Platinum Content (wt-%)	ERC Electrode Number	Nominal Platinum Loading (mg/cm ²)		Fabrication Method
				PTFE Content (wt-%)	PTFE Content (wt-%)	
ERC 202	3648-139A	15	7270	~0.65	40	Machine Rolled with 50% Carbon Black
ERC 203	3648-139A	15	7270	~0.65	40	Machine Rolled with 50% Carbon Black
ERC 204	3648-139A	15	7333	~0.80	50	Machine Rolled
ERC 205	3648-139A	15	7333	~0.80	50	Machine Rolled
ERC 206	50% 3648-139A 50% 3648-94A	15	7329	~0.55	45	Machine Rolled
ERC 207	50% 3648-139A 50% 3648-94A	15	7329	~0.55	45	Machine Rolled
ERC 208	50% 3648-139A 50% 3648-94A	15	7329	~0.55	45	Machine Rolled

Table XI (Cont'd.)
Kocite Electrode Characteristics

Cell Number	Kocite-Derived Electrocatalyst Batch	Platinum Content (wt-%)	ERC Electrode Number	Nominal		Fabrication Method
				Platinum Loading (mg/cm ²)	PTFE Content (wt-%)	
ERC 209	3648-153A	15	7603	~0.40	45	Machine Rolled
ERC 210	3648-153A	15	7603	~0.40	45	Machine Rolled
ERC 211	3648-153A	15	7796	~0.55	45	Machine Rolled
ERC 212	3648-153A	15	7796	~0.55	45	Machine Rolled
ERC 213	3648-153A	15	7796	~0.55	45	Machine Rolled
ERC 214	3648-153A	15	7975	~0.50	45	Machine Rolled
ERC 215	3648-143A	15		~0.50	45	Machine Rolled

Table XIIa

Cell Performance Results at 180°C

- Electro catalyst Batch 3648-94A -

Cell Number	Kocite-Derived Electrocatalyst Batch	Electrode Number	Nominal Platinum Loading (mg/cm^2)			Terminal Voltage @ 100 mA/cm^2 (mV)	@ 200 mA/cm^2 (mV)	Days Tested/ Peak Performance	Comments
			Air	Oxygen	Air				
ERC 160	3648-94A	4912	~0.60	610	680	500	600	2/1	Flooded
ERC 161	3648-94A	4912	~0.60	620	680	520	600	2/1	Flooded with Time
ERC 162	3648-94A	4914	~0.60	640	700	540	600	14/1	Flooded with Time
ERC 163	3648-94A	4914	~0.60	650	710	560	630	13/1	Flooded with Time
ERC 164	3648-94A	4914	~0.60	630	690	520	600	11/1	Flooded with Time
ERC 165	3648-94A	4912	~0.60	570	650	460	570	2/1	Flooded
ERC 166	3648-94A	5049	~0.60	620	695	525	620	6/1	Experimental Electrode
ERC 167	3648-94A	5050	~0.60	615	680	510	590	5/1	Experimental Electrode
ERC 169	3648-94A	4573	~0.55	640	700	560	630	12/1	Slight Decay
ERC 170	3648-94A	4574	~0.55	600	660	490	580	1/1	
ERC 171	3648-94A	4573	~0.55	630	685	540	615	3/1	Slight Decay
ERC 174	3648-94A	4921	~0.55	610	670	520	600	1/1	
ERC 175	3648-94A	4921	~0.55	640	700	560	640	40/1	Stable

Table XIIa (Cont'd)

Cell Performance Results at 180°C

- Electrocatalyst Batch 3648-94A -

Cell Number	Kocite-Derived Electrocatalyst Batch	Electrode Number	Nominal Platinum Loading (mg/cm ²)	Terminal Voltage @ 100 mA/cm ² (mV)	Days Tested/ Peak Performance	Comments
			Air Oxygen	Air Oxygen		
ERC 172	3648-94A	5400	~0.65	650	705	580
ERC 173	3648-94A	5403	~0.65	640	700	550
ERC 176	3648-94A	5401	~0.65	660	715	580
ERC 177	3648-94A	5047	~0.60	610	680	520
ERC 178	3648-94A	5401	~0.65	570	645	
ERC 179	3648-94A	5400	~0.60	640	700	560
ERC 180	3648-94A	5400	~0.60	670	725	600
ERC 181	3648-94A	5400	~0.60	600	670	510
ERC 182	3648-94A	5400	~0.60	650	700	570
ERC 183	3648-94A	5401	~0.65	660	720	590
ERC 184	3648-94A	5401	~0.65	630	690	540
UOP	3648-94A-1	5402	0.58	668	729	595
UOP	3648-94A-2	5402	0.58	658	576	664
UOP	3648-94A-3	5402	0.58	643	564	660
UOP	3648-94A-4	5402	0.58	649	714	576
UOP	3648-94A-5	5403	~0.60	641	713	557
UOP	3648-94A-6	5403	~0.60	713	810	644
ERC 185	3648-94A	5843	~0.60	635	690	560
ERC 186	3648-94A	5846	~0.65	620	680	520
ERC 187	3648-94A	5843	~0.60	620	680	525
ERC 188	3648-94A	5845	~0.65	660	710	590

The best cell performance results on a Kocite-derived electrocatalyst batch were obtained at ERC on batch 3648-115C as shown in Table XIIa (cell testing problems arose with this batch at UOP and cell testing was discontinued). The average cell performance at ERC was 590 mV with a standard deviation of 37 mV at 200 ma/cm² and 180°C on air. If the worst cell is discounted, the remaining 10 cells had an average performance of 599 mV with a standard deviation of 25 mV. The best cell performance achieved with this batch was 630 mV. Both the Pt dispersion determined by X-ray analysis and the performance of this batch in electrodes suggest that PDD impregnation produces a better electrocatalyst than CPA impregnation.

The performance of electrocatalyst 3648-118A was tested in a limited number of cells to determine if a lower Pt-loaded electrocatalyst and a thicker catalyst layer (keeping the same electrode Pt-loading) would give better cell performance. As indicated in Table XIIc, the results observed with this electrocatalyst are comparable to the results obtained with batch 3648-94A, suggesting no substantial improvement can be expected using lower Pt-loaded electrocatalysts.

The cell performance results obtained with electrodes from the Alon-derived electrocatalyst batch, 3648-139A, are given in Table XIIId. In general, cell performance was poor because ERC encountered substantial problems in trying to make electrodes from this very small particle material. The cells listed in Table XIIId contained electrodes with either a 1:1 mixture of carbon black and electrocatalyst 3648-139A or a 1:1 mixture of electrocatalyst batches 3648-94A and 3648-139A. In neither case was good cell performance obtained so this effort was terminated. However, with a substantially altered electrode structure this type of electrocatalyst may give much better performance.

Electrocatalyst batch 3648-153A appeared to be the best electrocatalyst made during this program. However, the results obtained with this batch indicated in Table XIIe, were not encouraging. ERC had some problems with electrodes made from this batch, due to the pyrophoric nature of this highly Pt-dispersed electrocatalyst. Electrocatalyst powder at the surface of the electrode was not well bonded to the electrode and could easily be rubbed off. This may have affected the electrode wetting characteristics and cell performance.

A polarization curve from cell ERC-201, containing Kocite electrodes prepared from electrocatalyst batch 3648-115C is shown in Figure 16. While these data are the best obtained on a cell with Kocite electrodes by ERC, its shape is characteristic of the polarization curves from good cells tested during this program. In Figure 17, the data for this cell are replotted on an IR free basis. The Tafel slope is about 85 mV per decade on oxygen and is linear at current densities

Table XIIb
 Cell Performance Results at 180°C
 - Electrocatalyst Batch 3648-115C -

Cell Number	Kocite-Derived Electrocatalyst Batch	Electrode Number	Nominal Platinum Loading (mg/cm ²)	Terminal Voltage (mV)		Days Tested/ Peak Performance	Comments
				@ 100 mA/cm ²	Air Oxygen		
ERC 189	3648-115C	6047	~0.65	630	690	545	605
ERC 190	3648-115C	6047	~0.65	680	730	620	680
ERC 191	3648-115C	6046	~0.60	670	720	580	650
ERC 194	3648-115C	6048	~0.60	680	730	610	670
ERC 195	3648-115C	6046	~0.60	600	660	500	560
ERC 196	3648-115C	6047	~0.65	680	740	610	680
ERC 197	3648-115C	6047	~0.65	680	740	610	670
UOP	3648-115C-1	6048	~0.60	595	681	538	607
UOP	3648-115C-2	6048	~0.60	590	652	498	569
UOP	3648-115C-3	6048	~0.60	597	665	517	592
UOP	3648-115C-4	6048	~0.60	626	626	538	540
UOP	3648-115C-5	6048	~0.60	622	622	540	540
UOP	3648-115C-6	6048	~0.60	629	629	543	543
UOP	3648-115C-7	6045	~0.60	649	649	573	573
UOP	3648-115C-8	6045	~0.60	652	652	575	575
UOP	3648-115C-9	6045	~0.60	631	693	548	618
UOP	3648-115C-10	6045	~0.60	622	699	541	623
UOP	3648-115C-11	6045	~0.60	643	707	562	632
UOP	3648-115C-12	6045	~0.60	690	690	630	690
ERC 198	3648-115C	6693	~0.60	680	740	610	670
ERC 199	3648-115C	6692	~0.65	670	730	600	670
ERC 200	3648-115C	6692	~0.65	640	700	570	630
ERC 201	3648-115C	6694	~0.65	690	740	630	690
ERC 198	3648-115C	6693	~0.60	680	740	610	670
ERC 199	3648-115C	6692	~0.65	670	730	600	670
ERC 200	3648-115C	6692	~0.65	640	700	570	630
ERC 201	3648-115C	6694	~0.65	690	740	630	690

Table XIIc
Cell Performance Results at 180°C
- Electrocatalyst Batch 3648-118A -

Cell Number	Kocite-Derived Electrocatalyst Batch	Electrode Number	Nominal Platinum Loading (mg/cm ²)		Terminal Voltage (mV)		@ 100 mA/cm ² Air Oxygen	@ 200 mA/cm ² Air Oxygen	Days Tested/ Peak Performance	Comments
			Air	Oxygen	Air	Oxygen				
ERC 192	3648-118A	6043	~0.65	660	715	580	640	10/2	Stable	
ERC 193	3648-118A	6043	~0.65	680	740	600	675	50/22	Stable	
UOP	3648-118A-1	6042	~0.60	627	696	536	622	1/1		
UOP	3648-118A-2	6042	~0.60	611		513		14/3		
UOP	3648-118A-3	6042	~0.60	626	691	537	611	11/8		
UOP	3648-118A-4	6042	~0.60	611		511		12/12		

Table XIIId
Cell Performance Results at 180°C
- Electrocatalyst Batch 3648-139A -

Cell Number	Kocite-Derived Electrocatalyst Batch	Electrode Number	Nominal Platinum Loading (mg/cm ²)		Terminal Voltage (mV) @ 100 mA/cm ²		Days Tested/ Peak Performance		Comments
			Air	Oxygen	Air	Oxygen	200 mA/cm ²	Oxygen	
ERC 202	3648-139A	7270	~0.65	630	710	540	640	4/1	Slight Flooding
ERC 203	3648-139A	7270	~0.65	580	680	480	620	1/1	Flooded
ERC 204	3648-139A	7333	~0.80	640	700	550	640	13/11	
ERC 205	3648-139A	7333	~0.80	640	710	560	640	6/5	
ERC 206	50% 3648-139A 50% 3648-94A	7329	~0.55	630	700	550	630	2/1	
ERC 207	50% 3648-139A 50% 3648-94A	7329	~0.55	620	700	540	620	1/1	
ERC 208	50% 3648-139A 50% 3648-94A	7329	~0.55	640	700	550	630	3/1	Stable

Table XIIe
Cell Performance Results at 180°C

- Electro catalyst Batch 3648-143A and -153A -

Cell Number	Kocite-Derived Electro catalyst Batch	Electrode Number	Nominal Platinum Loading (mg/cm ²)	Terminal Voltage (mV)		Days Tested/ Peak Performance	Comments
				@ 100 mA/cm ² Air	@ 200 mA/cm ² Oxygen		
ERC 209	3648-153A	7603	~0.40	640	700	560	630
ERC 210	3648-153A	7603	~0.40	640	700	570	640
ERC 211	3648-153A	7796	~0.55	620	680	540	600
ERC 212	3648-153A	7796	~0.55	620	690	530	600
ERC 213	3648-153A	7796	~0.55	640	700	550	640
ERC 214	3648-153A	7975	~0.50	640	700	550	620
ERC 215	3648-143A		~0.50	660	710	580	640

Slight Decay

60

Figure 16

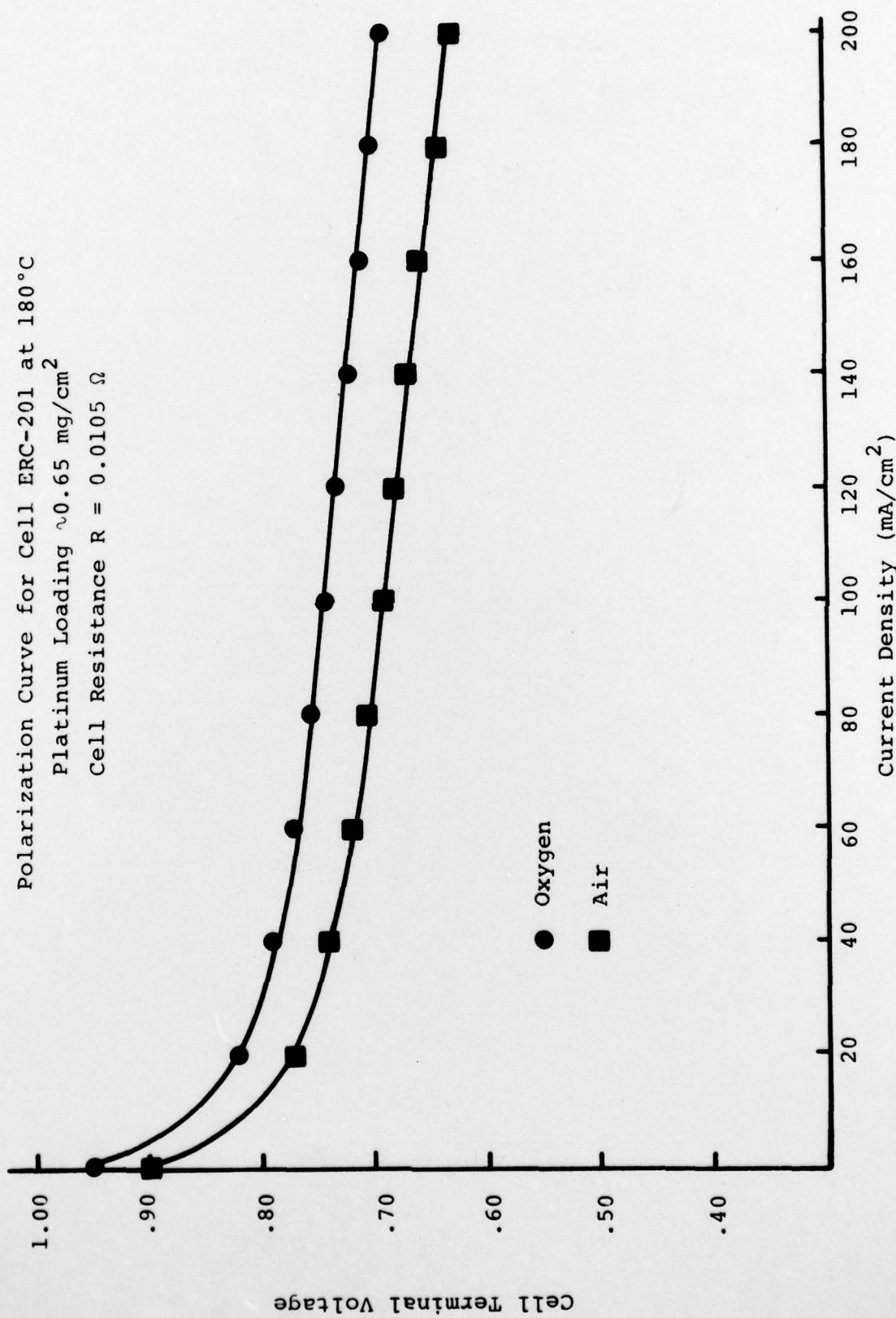
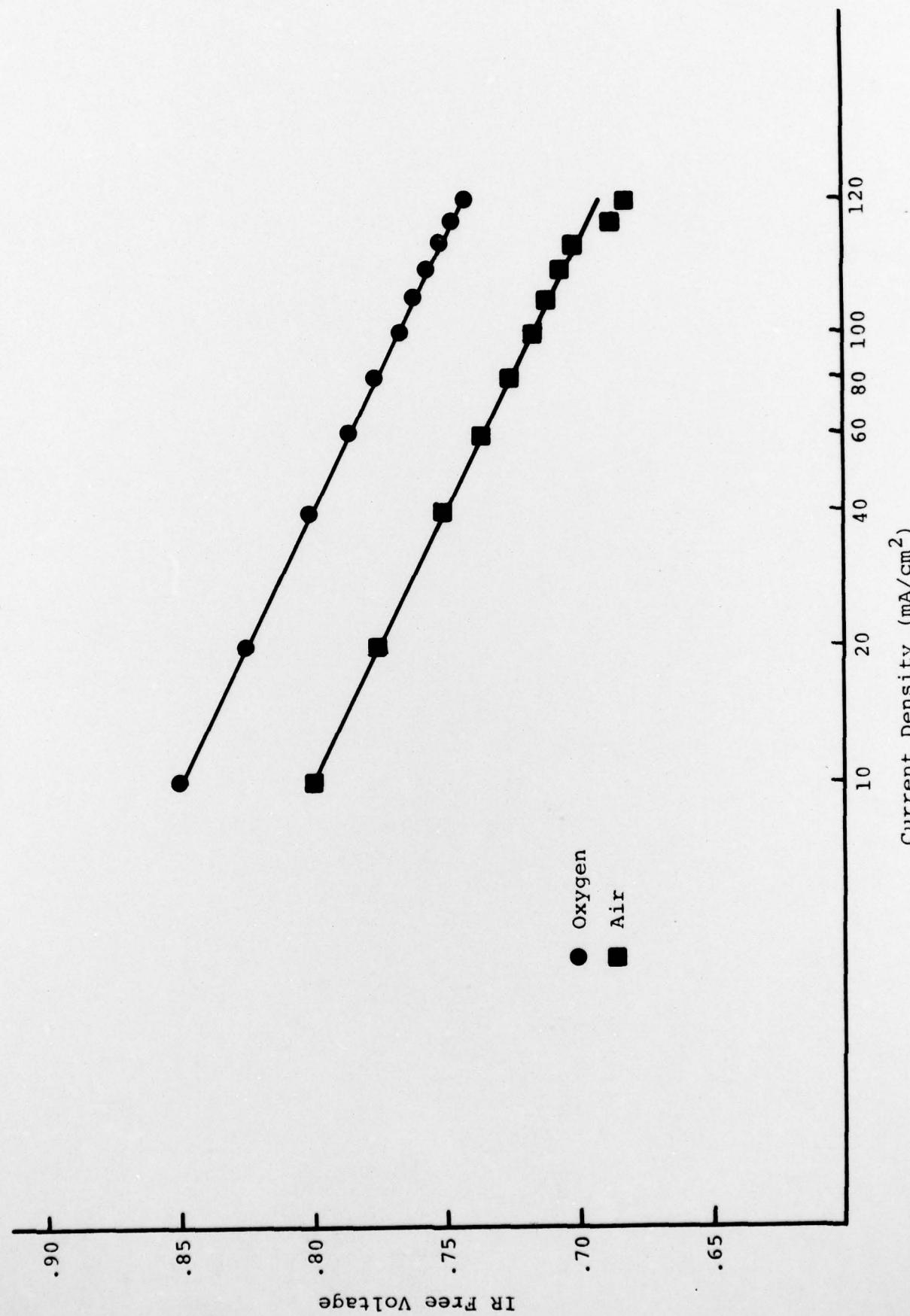


Figure 17

Polarization Curve for Cell ERC-201 at 180°C
Platinum Loading $\sim 0.65 \text{ mg/cm}^2$



up to 200 ma/cm^2 . The air Tafel slope is parallel to the oxygen Tafel slope at lower current densities, but some deviation occurs above 150 ma/cm^2 , probably as a result of small gas diffusional losses.

The Tafel slopes of cell ERC-201 are similar to those of other cells run during the program and are close to the theoretical prediction of 90 mV (2.30 RT/F) for porous acid fuel cell electrodes. From these data ERC concludes the anode polarization is nearly insignificant with cell performance being cathode controlled. The instability in anode performance observed earlier in the program was eliminated.

Since the program goals were primarily concerned with achieving a peak cell performance, relatively few cells were run longer than 1000 hrs. Cell endurance data of three cells assembled recently and tested for periods up to 5000 hrs. are shown in Figure 18, 19 and 20. In each case the performance is generally stable but a slight cell voltage decay is observable. In most cases, cell decay could not be clearly attributed to either the electrocatalyst or the electrode structure. Since cell decay generally occurred on both air and oxygen operation electrode flooding was apparently not the problem. Also cell decay appeared to occur mainly when a noticeable drop in the cell open circuit voltage was observed. This would indicate that cross gas leakage was a cell decay mechanism, a problem probably related to both the cell matrix and cell operating conditions.

Undoubtedly, some cell decay can be attributed to Pt recrystallization. Much of this decay should occur during the initial 100 hours of cell operation when Kocite electrodes are still filling with electrolyte. As a result, the expected initial rapid loss of Pt surface area, typical of other types of electrocatalysts, is probably not observable with the cells tested during this program. After 100 hours, the Pt recrystallization rate is expected to be much smaller, with cell decay during the endurance tests from this decay mechanism of probably less than 20 mV.

5.4 Summary of Results

The most important results obtained during the latest contract period are briefly summarized below.

A. Kocite-Derived Electrocatalyst Production

Kocite-derived electrocatalysts were produced using both leached Hydral 705-based Kocite material and leached Alon-based Kocite material in quantities of 50-100 grams. Both chloroplatinic acid and platinum diaminedinitrite were used as platinum sources with the platinum diaminedinitrite giving the highest Pt

Figure 18

Lifetime Test for Cell ERC-193 at 180°C
Platinum Loading $\approx 0.65 \text{ mg/cm}^2$

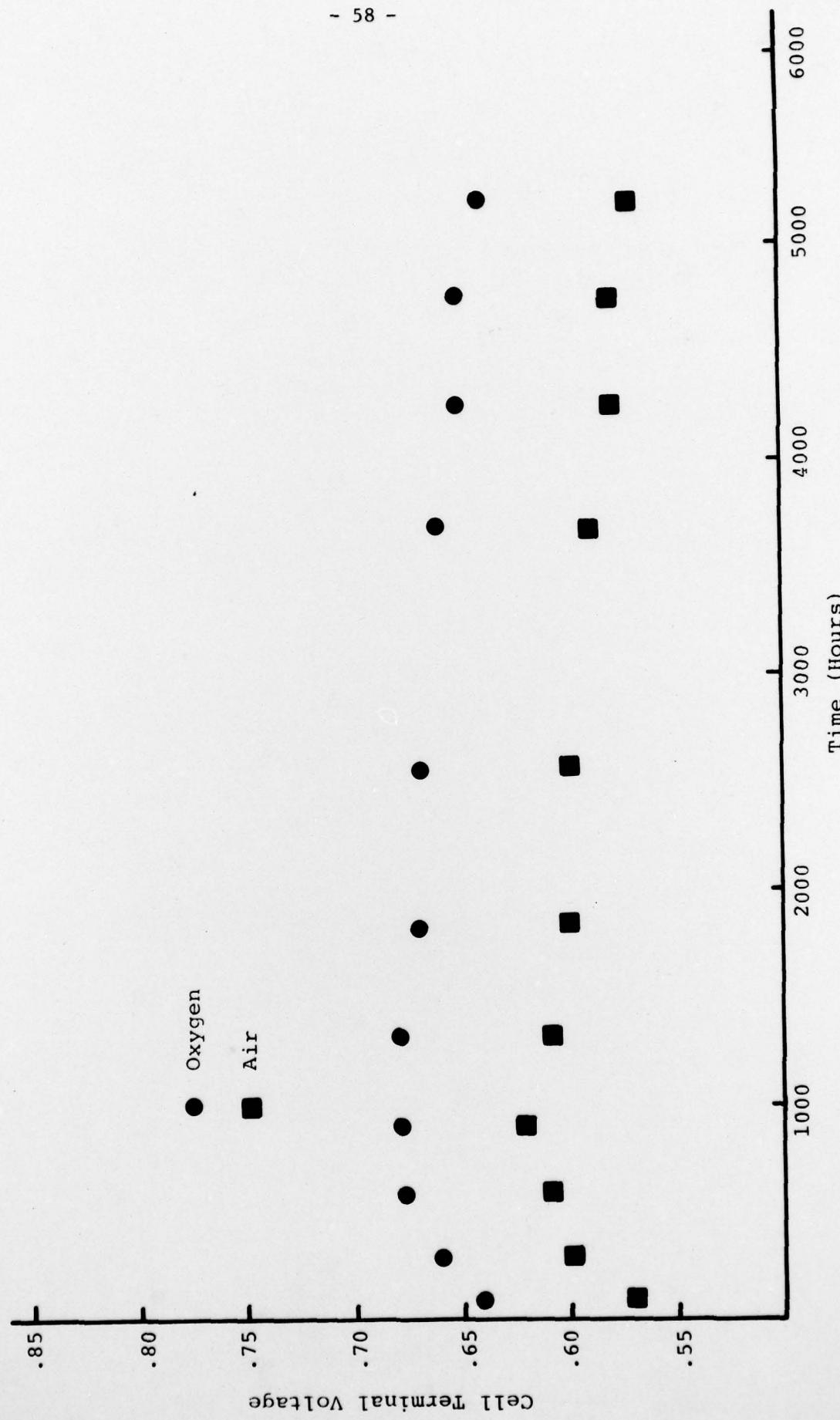


Figure 19

Lifetime Test for Cell ERC-193 at 180°C
Platinum Loading $\sim 0.65 \text{ mg/cm}^2$

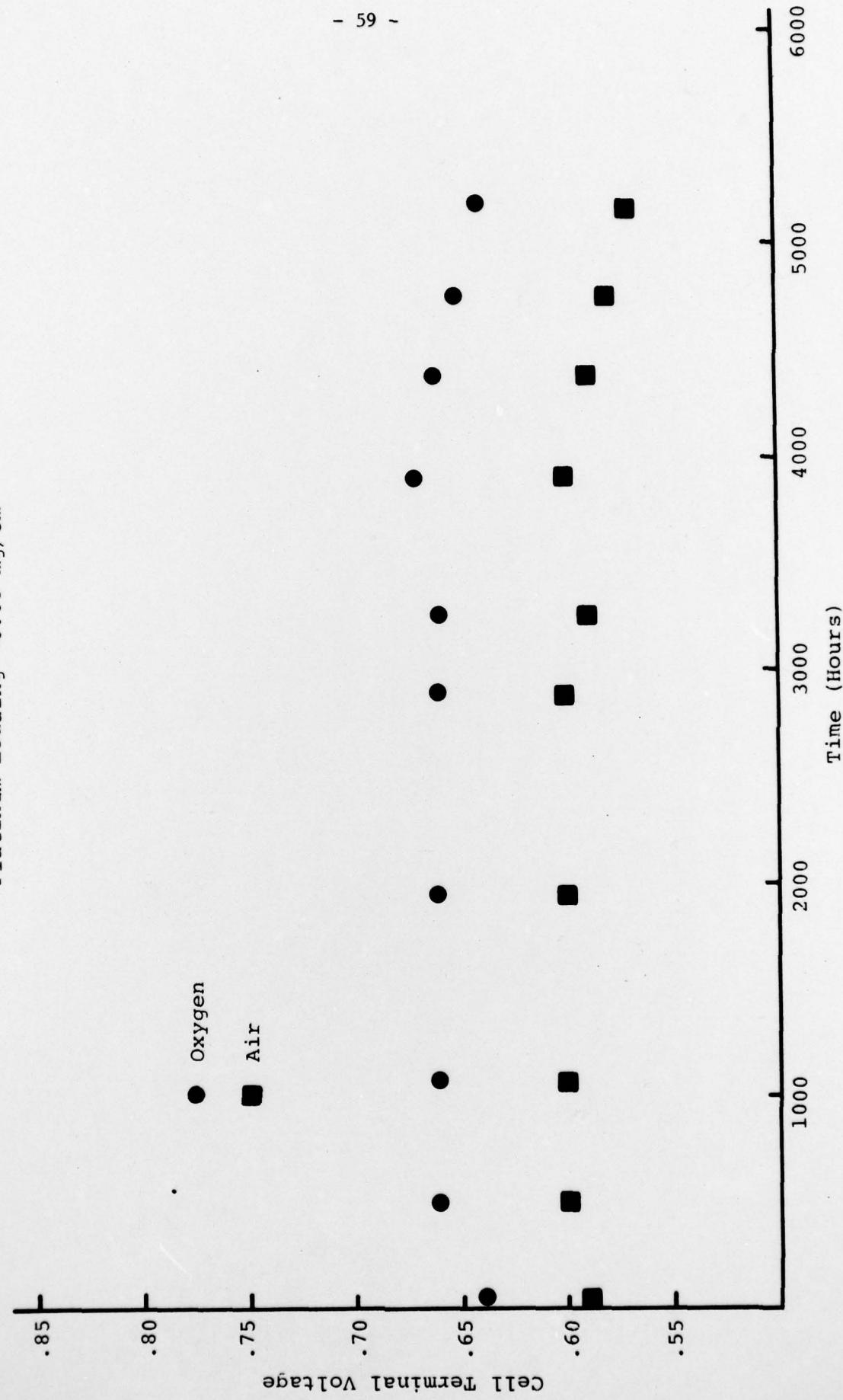
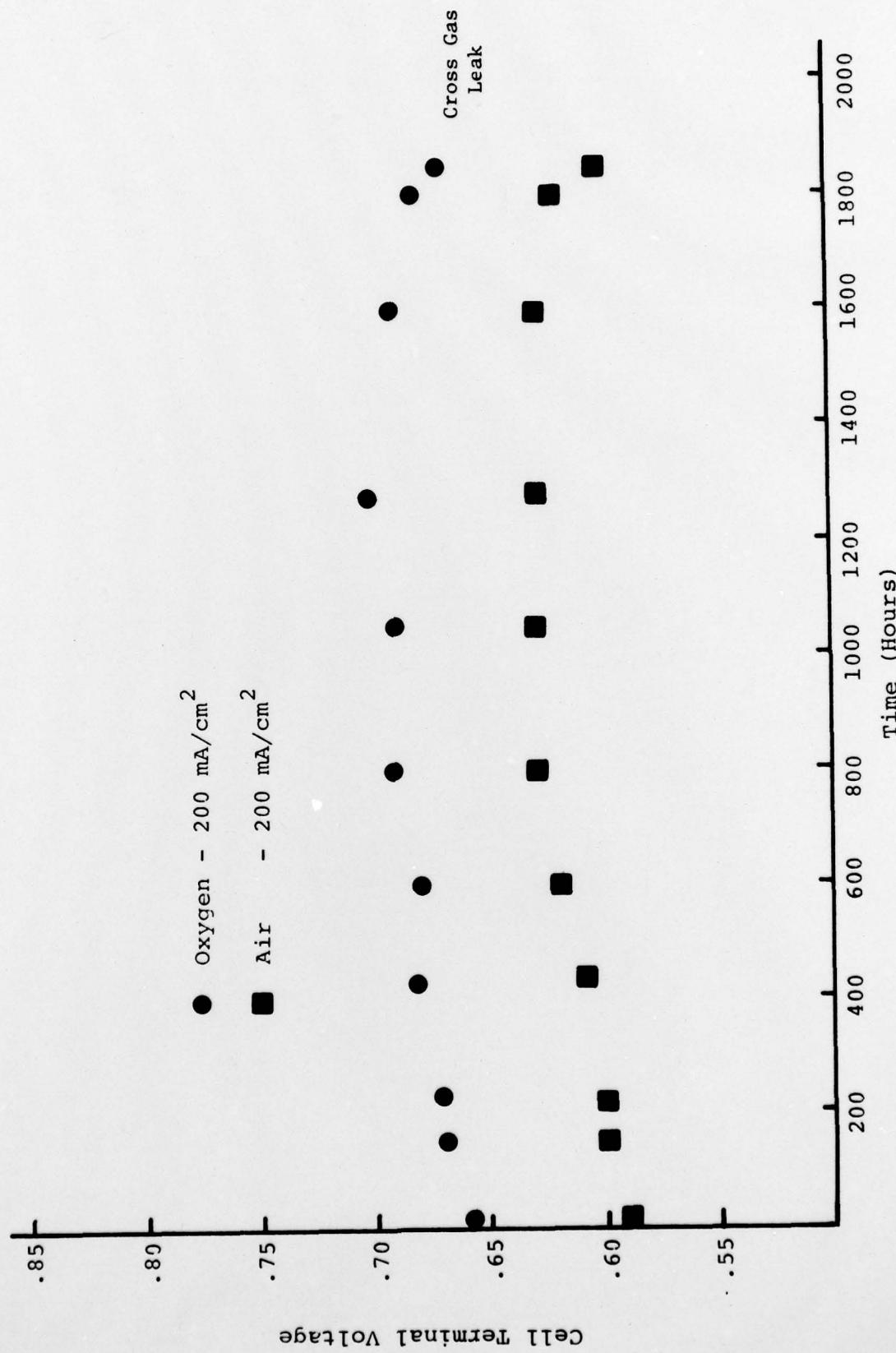


Figure 20

Lifetime Test for Cell ERC-201 at 180°C
Platinum Loading ~0.65 mg/cm²



dispersion as determined by Pt X-ray linewidth analysis. Three electrocatalysts, the PDD impregnated 3648-115C batch, the pre-oxidized PDD impregnated 3648-153A batch, and the CPA impregnated 3648-139A batch appear particularly promising. The first two batches were made from leached Hydral 705-based Kocite material and the latter used leached Alon-based Kocite material.

B. Kocite Electrode Performance

Kocite electrodes fabricated by machine rolling technique were used routinely as both cathodes and anodes. Cell performance results clearly demonstrated that Kocite electrodes having catalyst layer PTFE contents about 45 wt-% run stably as both anodes and cathodes.

The best results during this program were obtained with electrocatalyst 3648-115C. Over 60% of the cells constructed at ERC using Kocite electrodes fabricated from this batch had a performance level of 600 mV or higher at 200 ma/cm² and 180°C on air. The best cell reached 630 mV. Cells with these electrodes were still operating at 570 mV after 5000 hours.

The other two promising electrocatalyst types did not perform as well as the 3648-115C batch, even though the Pt dispersions were higher. The very small particle size of the 3648-139A batch was incompatible with ERC electrode fabrication techniques and batch 3648-153A was very difficult to handle during electrode fabrication because it was pyrophoric. It is possible that substantial modification of current ERC electrode fabrication techniques could produce Kocite electrodes superior to those produced during this program.

VI. CONCLUSIONS

Based on the results obtained during this program, and particularly during the last nine months, the following conclusions concerning low cost fuel cell electrodes fabricated from Kocite-derived electrocatalysts are warranted.

- (A) The optimum Kocite-derived electrocatalyst is produced by leaching the alumina from a Kocite material with hot H_3PO_4 , and then impregnating the resulting pyropolymer structure with platinum.
- (B) As judged by the performance of a Kocite-derived electrocatalyst in an ERC electrode structure, electrocatalysts prepared from Hydral 705-based Kocite materials had better performance than electrocatalysts prepared from Kaiser-based or Alon-based Kocite materials. However, preliminary electrocatalyst structure results indicate that Alon-based Kocite materials might, with the proper electrode structure modifications, be a superior electrocatalyst.
- (C) The best platinum dispersions and cell performance results were obtained using platinum diaminedinitrite as the platinum source. However, all platinum distributions measured show a bimodal particle size variation and a non-uniform support particle loading.
- (D) Kocite electrodes fabricated by the ERC machine rolling method proved to have more reproducible performance than those fabricated by the more experimental sheet mold technique. With this technique electrode performance is less affected by small differences among electrocatalyst batches.
- (E) Endurance testing of Kocite electrodes in excess of 5000 hours indicated the electrocatalysts and anodes perform stably as air or oxygen cathodes and hydrogen anodes in H_3PO_4 electrolyte cells at 180°C. Although platinum recrystallization probably occurs during cell operation, leading to slightly lower cell voltage, no severe cell decay mechanism appears to result from electrocatalyst fabrication. Corrosion of the leached Kocite material did not appear to be a problem under the test conditions used in this program.
- (F) The principle advantage of using Kocite-derived Pt supports results from an ability to separately control the pore size distribution, particle size, and chemical nature of the support material. Thus it is possible to customize Kocite-derived supports to obtain the optimal blend of these properties. Throughout this program only a few of the many possible Kocite-derived electrocatalyst variants have been prepared and evaluated, with a Hydral 705-based variant receiving the most attention. As a clearer understanding of the optimal support properties for H_3PO_4 acid cell applications is developed, further optimization of Kocite-derived electrocatalysts can be made by taking advantage of the flexibility in the choice of chemical and structural properties available with Kocite-derived supports.

VII. RECOMMENDATIONS

- (A) Further efforts should be made to achieve more uniform platinum distributions from particle to particle and a less bimodal platinum size distribution.
- (B) Kocite electrodes of modified structure should be fabricated using Kocite-derived electrocatalysts made from Alon-based Kocite material. Optimization of electrode structures incorporating this type of electrocatalyst may produce an electrode superior to the best Kocite electrodes prepared during this program.
- (C) For the Hydral-based electrocatalysts, the cathode electrode structure appears to be reasonably optimized. However, further effort in optimizing anodes is probably warranted. Such effort should include lowering the anode Pt loading to 0.25 mg/cm^2 and determining the optimum PTFE content to give maximum anode carbon monoxide tolerance.
- (D) The optimum electrocatalyst platinum content has not been precisely determined. Reducing the electrocatalyst platinum content below 15 wt-% and increasing the electrode thickness might prove advantageous.
- (E) Long-term endurance testing of Kocite electrodes at high temperatures may be aided with improved matrix structures such as SiC.
- (F) An ERC analysis of cell performance data tends to indicate that a significant portion of the platinum within an electrode is probably not being utilized. Improvements in the wetting behavior of either the electrocatalyst or electrode structure could result in significant performance increases.

VIII. REFERENCES

1. L. B. Welsh, R. W. Leyerle, G. L. Hervert and K. J. Youtsey, "Carbonaceous Catalysts for H_3PO_4 Fuel Cells", MERDC Contract DAAK02-75-C-0011, Final Technical Report, September, 1975.
2. L. B. Welsh, R. W. Leyerle, G. L. Hervert, "Optimization of Pt-Doped Kocite^R Electrodes in H_3PO_4 Fuel Cells", MERADCOM Contract DAAG53-76-C-0014, Interim Technical Report, March, 1976.
3. L. B. Welsh, R. W. Leyerle, "Optimization of Pt-Doped Kocite^R Electrodes in H_3PO_4 Fuel Cells", MERADCOM Contract DAAG53-76-C-0014, Interim Technical Report, August, 1976.
4. L. B. Welsh, R. W. Leyerle, "Optimization of Pt-Doped Kocite^R Electrodes in H_3PO_4 Fuel Cells", MERADCOM Contract DAAG53-76-C-0014, Interim Technical Report, January, 1977.
5. L. B. Welsh, R. W. Leyerle, "Optimization of Pt-Doped Kocite^R Electrodes in H_3PO_4 Fuel Cells", MERADCOM Contract DAAG53-76-C-0014, Interim Technical Report, January, 1978.
6. L. B. Welsh, R. W. Leyerle and D. M. Preston, "Optimization of Pt-Doped Kocite^R Electrodes in H_3PO_4 Fuel Cells", MERADCOM Contract DAAG53-76-C-0014, Interim Technical Report, August, 1978.
7. TEM results obtained with the cooperation of Professor A. V. Crewe and Mitsuo Ohtsuki at the University of Chicago.

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